
**Natural gas — Supporting information
on the calculation of physical
properties according to ISO 6976**

*Gaz naturel — Informations supplémentaires pour le calcul des
propriétés physiques selon l'ISO 6976*

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Contents

	Page
Foreword.....	vi
Introduction.....	vii
1 Scope.....	1
2 Normative references.....	1
3 Terms and definitions.....	1
4 Symbols, units and abbreviated terms.....	1
4.1 Quantities.....	1
4.2 Subscripts.....	3
4.3 Superscripts.....	3
4.4 Abbreviated terms.....	3
5 Enthalpy of combustion of the ideal gas and its variation with temperature.....	4
5.1 Preamble.....	4
5.2 Standard enthalpy of combustion at 25 °C.....	4
5.3 Standard enthalpy of combustion at other temperatures.....	5
5.4 Formulation of the ideal-gas enthalpy.....	6
5.5 Illustrative examples.....	7
5.6 Uncertainty in enthalpy of combustion.....	8
6 Non-ideality: Variation of real-gas enthalpy of combustion with pressure.....	9
6.1 Preamble.....	9
6.2 Formulation of the enthalpic correction.....	10
6.3 Estimation of the enthalpic correction.....	12
6.4 Conclusion.....	13
7 Non-ideality: Compression factor effect on volume-basis calorific values.....	13
7.1 Compression factor.....	13
7.2 Virial equation of state.....	14
7.3 Estimation of mixture compression factor.....	15
7.4 Limitations of the modified IGT-32 method.....	17
7.5 Uncertainty in compression factor.....	18
8 Quantitation of volumetric non-ideality.....	18
8.1 Second virial coefficients of pure components.....	18
8.1.1 Preliminary procedures.....	18
8.1.2 Improved procedure.....	19
8.2 Summation factors of pure components.....	21
8.2.1 Overview.....	21
8.2.2 Major components of natural gas.....	21
8.2.3 Hydrogen and helium.....	22
8.3 Compression factors of the permanent gases.....	23
8.4 Pure component uncertainties.....	25
8.4.1 Uncertainty of second virial coefficients.....	25
8.4.2 Truncation error.....	25
8.4.3 Linearization error.....	27
8.4.4 Berlin versus Leiden.....	28
8.4.5 Hydrogen and helium.....	29
8.4.6 Water.....	30
8.4.7 Combination of uncertainties.....	31
8.5 Mixture uncertainty.....	31
9 Miscellaneous data.....	31
9.1 Atomic weights of the elements.....	31
9.1.1 Atomic weights 2007.....	31
9.1.2 Atomic weights 2009 and 2011.....	32
9.1.3 Discussion.....	34

9.2	Composition and molecular weight of dry air	35
10	Effects of water vapour on calorific value	36
10.1	Preamble	36
10.2	Excluded volume effect	37
10.3	Latent heat (enthalpic) effect	38
10.4	Compression factor effect	39
10.5	Combination of effects	39
10.6	Spectator water	40
10.7	Effect of humid air	41
10.7.1	Preamble	41
10.7.2	Stoichiometric combustion with oxygen	42
10.7.3	Combustion of dry gas with excess dry air	42
10.7.4	Combustion of wet gas with excess dry air	43
10.7.5	Combustion of wet gas with excess humid air	43
11	Summary, discussion and selection of the calorific value of methane	45
11.1	Standard enthalpy of combustion	45
11.1.1	Background	45
11.1.2	Selection of data	45
11.1.3	Recalculation of Rossini values	46
11.1.4	Evaluation of selected data	48
11.1.5	Selected value and uncertainty	52
11.2	Derived calorific values	52
11.3	Comparisons between calorimetric methodologies	54
12	Calorific values on a mass basis	56
12.1	Calorific values on a mass basis for components of natural gas	56
12.2	Alternative (non-normative) method of calculation for mass-basis calorific values	57
13	Calorific values on a volume basis	60
13.1	Calorific values on a volume basis for components of natural gas	60
13.2	Alternative (non-normative) method of calculation for volume-basis calorific values	60
14	Approximate conversion between reference conditions	63
14.1	Factors for conversion between metric reference conditions	63
14.2	Equations for conversion between metric reference conditions	65
14.3	Expression of non-SI reference (base) pressures in metric units	65
15	Mathematical and methodological issues relating to estimation of uncertainty	66
15.1	Principles	66
15.2	Input data	68
15.2.1	Preamble	68
15.2.2	Reference conditions	68
15.2.3	Composition data	68
15.2.4	Physical property data	69
15.3	Uncertainty of the calculational method	70
15.4	Evaluation of sensitivity coefficients	70
15.4.1	Preamble	70
15.4.2	Analytical method	71
15.4.3	Finite difference method	73
15.4.4	Monte Carlo method	73
16	Detailed derivation of uncertainty equations in ISO 6976:2016	73
16.1	Principles and assumptions	73
16.2	General formulation	74
16.3	Effects of correlations	75
16.3.1	Correlation between mole fractions	75
16.3.2	Correlation between molar masses	76
16.3.3	Correlation between physical properties	78
16.4	Uncertainty equations for basic properties	78
16.4.1	Molar mass	78

16.4.2	Molar-basis gross calorific value.....	79
16.4.3	Molar-basis net calorific value.....	79
16.4.4	Summation factor.....	80
16.4.5	Compression factor.....	80
16.5	Uncertainty equations for compound properties.....	81
16.5.1	Mass-basis gross calorific value.....	81
16.5.2	Mass-basis net calorific value.....	82
16.5.3	Volume-basis gross calorific value.....	83
16.5.4	Volume-basis net calorific value.....	84
16.5.5	Density.....	86
16.5.6	Relative density.....	87
16.5.7	Gross Wobbe index.....	88
16.5.8	Net Wobbe index.....	89
16.6	Repeatability and reproducibility.....	91
17	Computer implementation of recommended methods.....	92
17.1	Compiled BASIC shareware program.....	92
17.2	Spreadsheet implementation.....	94
	Bibliography.....	97

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

Introduction

Both international and intranational custody transfer of natural gas usually require precise determination of both the quantity and the quality of the gas to be traded. ISO 6976:2016, which cancels and replaces ISO 6976:1995, specifies methods for the calculation of those properties, often known as the combustion properties, which (in part) describe gas quality, namely gross (superior) and net (inferior) calorific value, density, relative density, gross and net Wobbe index. The methods provide the means of calculating the properties, including uncertainties, of any natural gas, natural gas substitute, or similar combustible gaseous fuel of known composition at commonly used reference conditions.

Some 80-odd years ago, in the Introduction to Hyde and Mills' classic text *Gas Calorimetry*, Sir Charles Vernon ('CV') Boys wrote the words^[109] " ... I hesitate to give the number of actual tests of the calorific value of gas which are made every year, but ... it will be evident that any machinery set up to ascertain its value must be extensive ... The fact is that no single commodity generally purchased by the public is so carefully watched and maintained of its guaranteed quality as gas ... ". Since that time, the technology of gas calorimetry has changed beyond either recognition or imagination, but the truth of the sentiment expressed remains unchanged and refers every bit as much to 2017 as it did to 1932.

This document acts as a repository for those manifold technical details which justify and explain the methods presented in the new third (2016) edition of ISO 6976 but which are not directly needed in its everyday routine implementation. In short, it is conceived and intended as a complete(ish) knowledge base which provides full and proper technical authentication of ISO 6976.

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Natural gas — Supporting information on the calculation of physical properties according to ISO 6976

1 Scope

This document acts as a repository for those manifold technical details which justify and explain the methods presented in the third edition of ISO 6976 but which are not directly needed in the everyday routine implementation of the standard.

Each main clause addresses a specific aspect of the calculational method described in ISO 6976:2016, and is intended to be self-sufficient and essentially independent of each other clause. For this reason, the user should not expect the whole to be accessible to study as a sequentially coherent narrative.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6976 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

4 Symbols, units and abbreviated terms

4.1 Quantities

Symbol	Meaning	Unit
a	atomic index for carbon in the generalized molecular species $C_aH_bN_cO_dS_e$	—
b	atomic index for hydrogen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
c	atomic index for nitrogen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
d	atomic index for oxygen in the generalized molecular species $C_aH_bN_cO_dS_e$	—
e	atomic index for sulfur in the generalized molecular species $C_aH_bN_cO_dS_e$	—
g	coefficients in equation for B	—
h	molar enthalpy	$\text{kJ}\cdot\text{mol}^{-1}$
k	coverage factor	—
m	number of sets of values	—
n	number of determinations in a set of values	—
p	pressure (absolute)	kPa
q	exact input quantity in calculation of Y	(varies)
r	correlation coefficient	—
s	summation factor	—
t	Celsius temperature	$^{\circ}\text{C}$
$u(Y)$	standard uncertainty of Y	(varies)

Symbol	Meaning	Unit
$u(Y, Y')$	covariance of Y and Y'	(varies)
w	repeatability or reproducibility	(varies)
x	mole fraction	—
y	inexact input quantity in calculation of Y	(varies)
A	atomic mass (atomic weight)	$\text{kg}\cdot\text{kmol}^{-1}$
B	second virial coefficient	$\text{m}^3\cdot\text{mol}^{-1}$
C	third virial coefficient	$\text{m}^6\cdot\text{mol}^{-2}$
C_p	molar isobaric heat capacity	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
D	(mass) density	$\text{kg}\cdot\text{m}^{-3}$
\bar{D}	molar density	$\text{mol}\cdot\text{m}^{-3}$
E	non-random (systematic) bias from the true value of H_c	$\text{kJ}\cdot\text{mol}^{-1}$
F	function that generates property Y	—
G	relative density	—
H_c	molar-basis calorific value (negative enthalpy of combustion)	$\text{kJ}\cdot\text{mol}^{-1}$
H_f	enthalpy of formation	$\text{kJ}\cdot\text{mol}^{-1}$
H_m	mass-basis calorific value	$\text{MJ}\cdot\text{kg}^{-1}$
H_v	volume-basis calorific value	$\text{MJ}\cdot\text{m}^{-3}$
J	j -th virial coefficient	$\text{m}^{3(j-1)}\cdot\text{mol}^{-(j-1)}$
L	molar enthalpy of vaporization of water	$\text{kJ}\cdot\text{mol}^{-1}$
M	molar mass (molecular weight)	$\text{kg}\cdot\text{kmol}^{-1}$
N	number of components in a mixture	—
	number of input values of y	—
Q	amount of heat released	$\text{kJ}\cdot\text{mol}^{-1}$
R	molar gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
S	sum of mole fractions (= 1)	—
T	thermodynamic (absolute) temperature	K
$U(Y)$	expanded uncertainty of Y	(varies)
V	molar volume	$\text{m}^3\cdot\text{mol}^{-1}$
W	Wobbe index	$\text{MJ}\cdot\text{m}^{-3}$
Y	general (unspecified) physical property	(varies)
Z	compression factor	—
α	mole fraction of nitrogen in dry combustion air	—
β	mole fraction of oxygen in dry combustion air	—
γ	mole fraction of argon in dry combustion air	—
δ	mole fraction of water vapour in humid combustion air	—
ε	molar amount of air (including any excess) per mole of reactant	—
ζ	zero-value parameter having non-zero uncertainty	—
η	unity-value factor having non-zero uncertainty	—
θ	$a + b/4$	—
λ	random contribution of offset from the true value of H_c	$\text{kJ}\cdot\text{mol}^{-1}$
μ	dipole moment	debyes
ν	stoichiometric coefficient	—
ξ	relative humidity	—
τ	$100\text{ K}/T$	—
φ	molar amount of saturated exhaust gases per mole of reactant	—

Symbol	Meaning	Unit
ω	acentric factor	—
A_{1-9}	constants in the Aly-Lee Cp^o formulation	—
Φ	function that generates the third term of a virial expansion	—

4.2 Subscripts

c	at the gas-liquid critical point
g	for the sample gas
i	serial counter
	component identifier
j	serial counter
	component identifier
k	serial counter
m	serial counter
n	serial counter
r	value made dimensionless (reduced) using values for the gas-liquid critical properties
s	at the vapour-liquid saturation point
w	for water vapour
G	gross/superior (calorific value or Wobbe index)
N	net/inferior (calorific value or Wobbe index)
air	for air
0	reference (base) value of pressure or temperature
1	combustion reference state/condition
2	metering reference state/condition

4.3 Superscripts

o	for the ideal gas state
$*$	pre-normalization value
$+$	modified value

4.4 Abbreviated terms

liq	liquid
ppm	parts per million (moles per million moles)
sat	saturated with water vapour
vap	vapour
AGA	American Gas Association (USA)
BAM	Bundesanstalt für Materialforschung und Prüfung (Germany)
BBC	British Broadcasting Corporation (UK)
CIAAW	IUPAC Commission on Isotopic Abundances and Atomic Weights
GERG	Groupe Européen de Recherches Gazières
GOMB	Gas and Oil Measurement Branch (UK Department of Energy)
GPA	Gas Processors Association (USA)
IAPWS	International Association for the Properties of Water and Steam
IGT	Institute of Gas Technology (USA)
IUPAC	International Union of Pure and Applied Chemistry

NAMAS	National Measurement Accreditation Service (UK)
NBS	National Bureau of Standards (U.S. Department of Commerce)
NIST	National Institute of Standards and Technology (U.S. Department of Commerce)
NPL	National Physical Laboratory (UK)
OFGEM	Office of Gas and Electricity Markets (UK National Regulatory Authority)
PTB	Physikalische-Technische Bundesanstalt (Germany)
PVT	pressure-volume-temperature
SD	standard deviation
SE	experimental standard deviation of the mean (standard error)
SI	Système Internationale des Unités
UKAS	United Kingdom Accreditation Service (UK)

5 Enthalpy of combustion of the ideal gas and its variation with temperature

5.1 Preamble

The most fundamental thermophysical properties required in the calculation of the calorific values of a gas or gas mixture are the ideal-gas (standard) enthalpies of combustion $(-Hc^o)_j$ of each of its component molecular species at any temperature at which combustion may be deemed to take place, i.e. the combustion reference temperature.

In ISO 6976:2016, 6.1, the user is advised that each of these quantities $(-Hc^o)_j$, equal numerically to the corresponding ideal-gas gross (superior) calorific value $(Hc^o)_G^o$ of component j varies, albeit weakly, with the combustion reference temperature. The variation observed is nevertheless significant and cannot be ignored in the kind of high-precision calculations that are made possible by ISO 6976.

The theoretical variation of Hc^o with temperature is in general mathematically unwieldy and, in consequence, it is not practicable to provide simple formulations that would enable the user to determine Hc^o at any arbitrary combustion reference temperature. Instead, values of $(Hc^o)_j$ for each distinct molecular species j listed in ISO 6976 are given in ISO 6976, Table 3 for each of the commonly used combustion reference temperatures of 298,15 K, 293,15 K, 288,71 K, 288,15 K and 273,15 K (25 °C, 20 °C, 60 °F, 15 °C and 0 °C, respectively).

The first of these temperatures, 298,15 K, is the temperature adopted by the International Union of Pure and Applied Chemistry (IUPAC) as the reference temperature for thermochemistry and, in consequence, critically evaluated values of $Hc^o(25)$ are readily available in the published scientific literature.

Values of Hc^o have therefore been carefully selected for each of the chemical species listed in ISO 6976:2016 at this temperature (see 5.2), and used as the basis for the calculation of values for the other temperatures as described below (see 5.3 and 5.4).

5.2 Standard enthalpy of combustion at 25 °C

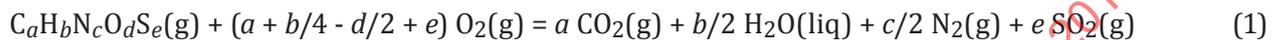
Except for methane, for which a new and specially detailed re-evaluation is given in [Clause 11](#) and for water (changed by a trivially small amount in accordance with the latest IAPWS documentation^[3]), the values of $Hc^o(25)$ listed in ISO 6976:2016, Table 3 are unchanged from those given in ISO 6976:1995. All of these values were, in turn, taken from fully-referenced tabulations in GERG TPC/1^[4], the major sources for which were Garvin et al.^[5] and tables published by the Thermodynamics Research Center^[6].

For those components new to the third edition of ISO 6976, namely n-undecane, n-dodecane, n-tridecane, n-tetradecane and n-pentadecane, values of $Hc^o(25)$ have been taken without change from [6].

5.3 Standard enthalpy of combustion at other temperatures

The values listed in ISO 6976:2016, Table 3 for temperatures other than 25 °C have been derived as follows.

Consider the generalized combustion reaction for the pure, supposedly gaseous, chemical species $C_aH_bN_cO_dS_e$, in which the atomic indices a to e are small non-negative integers (including zero) whose values define the specific species in question (e.g. for $a = 1, b = 4, c = d = e = 0$, the species is CH_4), viz.



NOTE In some applications, it might be better to consider any sulfur in the products of combustion to be present as H_2SO_4 , either gaseous or liquid as appropriate but, in the present application, gaseous sulfur dioxide is the likely product.

Suppose that the standard enthalpy of combustion at 25 °C, $-Hc^o(25)$, for this reaction is available in authoritative publications (as is indeed the case for all species considered herein). The value of $Hc^o(t)$ at some other temperature t , for this same species j , is then given by

$$[-Hc^o(t)]_j = [-Hc^o(t_0)]_j + \sum_i v_i \times [h_i^o(t_0) - h_i^o(t)] \quad (2)$$

or, equivalently,

$$[-Hc^o(t)]_j = [-Hc^o(t_0)]_j + \sum_i \int_t^{t_0} v_i \times (Cp_i^o) dt \quad (3)$$

where

t_0 is equal to 25 °C;

$h_i^o(t)$ is the ideal-gas molar enthalpy of component i ;

$(Cp^o)_i$ is the ideal-gas isobaric molar heat capacity of component i (except for product water which is taken as the liquid);

v_i is the stoichiometric coefficient for component i , being taken as positive for reactants (unity for the "object" species j) and negative for products.

The summation is taken over all species i (including j) that appear in the combustion reaction (a maximum of 6 in the most general case).

For convenience, we may set

- $i = 1$ for the combusted species j , from which it follows that $v_1 = 1$ for all j ,
- $i = 2$ for the reactant oxygen, whence $v_2 = [a+(b/4)-(d/2)+e]$,
- $i = 3$ for the product carbon dioxide, whence $v_3 = -a$,
- $i = 4$ for the product water, whence $v_4 = -b/2$,
- $i = 5$ for any product nitrogen, whence $v_5 = -c/2$, and
- $i = 6$ for any product sulfur dioxide, whence $v_6 = -e$.

Thus, the calculation is reduced to having sufficient knowledge of either h^o or, equivalently, Cp^o as a function of temperature, for the “object” species j and for the 5 “auxiliary” species O_2 , CO_2 , N_2 and SO_2 (in the gas phase) and liquid water. Either quantity is a complicated function of temperature, historically often expressed in polynomial form, for all molecular species.

5.4 Formulation of the ideal-gas enthalpy

Appropriate data for the enthalpy differences $[h_i^o(t_0) - h_i^o(t)]$ between specific temperatures, which thus enable direct calculations of $Hc^o(t)$, without recourse to polynomial expressions, may be found for several of the present components in the compilations of Armstrong and Jobe^[2] and (less explicitly) of Garvin et al.^{[5][8]} For components not considered in these sources recourse is indeed necessary to polynomial expressions that are available in the research literature.

Several types of polynomial expression have been used over the years to represent the variation of h^o and Cp^o with temperature. For the present application, the temperature range over which the variation is needed is rather small (a maximum of 25 K). Partially as a consequence of this, the entire second term on the right-hand side of [Formulae \(2\)](#) and [\(3\)](#) is very small by comparison with the leading term, and any reasonable formulation should produce essentially identical results for $Hc^o(t)$. Polynomials of the simple functional form given by Passut and Danner^[9] (a power series in absolute temperature T) or of the somewhat more complex modified Wilhoit-Harmens form^{[10][11][12]} are available for a very wide range of molecular species.

For preliminary investigations in ISO 6976:1995, calculations for $Hc^o(t)$ were, wherever possible, carried out by a variety of routes in order to confirm their equivalence. No significant discrepancies were revealed - that is, differences were generally only to be found at the level of hundredths of $\text{kJ}\cdot\text{mol}^{-1}$ (the second place of decimal in ISO 6976:2016, Table 3). This level of uncertainty is usually not significant in terms of either measurement accuracy or the required precision of calculation, and the second place of decimal is retained in Table 3 only for interpolative purposes.

Since somewhat before (but not used in) the preparation of the second edition of ISO 6976, a more complex formulation for $h^o(T)$ and $Cp^o(T)$ has become available through the publications of Lee et al.^{[13][14][15]}, reproduced here for Cp^o as [Formula \(4\)](#).

$$\frac{Cp^o(T)}{R} = \Lambda_1 + \Lambda_2 \cdot \left(\frac{\Lambda_3 / T}{\sinh(\Lambda_3 / T)} \right)^2 + \Lambda_4 \cdot \left(\frac{\Lambda_5 / T}{\cosh(\Lambda_5 / T)} \right)^2 + \Lambda_6 \cdot \left(\frac{\Lambda_7 / T}{\sinh(\Lambda_7 / T)} \right)^2 + \Lambda_8 \cdot \left(\frac{\Lambda_9 / T}{\cosh(\Lambda_9 / T)} \right)^2 \quad (4)$$

This formulation, involving the use of hyperbolic functions, has gained much popularity and has been applied to many components of natural gas by Jaeschke and Schley^[16], who give values of the constants Λ_{1-9} for each of these components. Furthermore, it has been incorporated into the methodology given in ISO 20765-1:2005^[17] and ISO 20765-2:2015^[18] for the calculation of thermodynamic properties of natural gas.

For this reason, the Aly-Lee method, as implemented in the commercially available thermophysical properties computer package GasVLe^{®1)}, has been used for the purpose of deriving final values of $Hc^o(20)$, $Hc^o(15,55)$, $Hc^o(15)$ and $Hc^o(0)$ from $Hc^o(25)$ to list in ISO 6976:2016, Table 3. In general, the values so derived are unchanged from those listed in ISO 6976:1995, Table 3, but in a few cases there are trivial changes of one or two hundredths of $\text{kJ}\cdot\text{mol}^{-1}$.

1) GasVLe[®] is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

5.5 Illustrative examples

Figure 1 is an example, in this case for methane, of how conversion from standard enthalpy of combustion at 25 °C (assumed known) to the corresponding value at 15 °C is carried out. The calculation is performed in accordance with Formula (2) and is presented in Figure 1 in a simple flowsheet-cum-spreadsheet style layout. All the values of $[h^0(25) - h^0(15)]$ are taken directly from tabulations given in Armstrong and Jobel^[7]. No further explanation seems to be necessary.

Another example is given as Figure 2, in this case for hydrogen sulfide, a non-hydrocarbon for which not all of the required data are available in Armstrong and Jobe. This time the conversion is carried out from 25 °C to 0 °C. In this example, of course, the products include sulfur dioxide but no carbon dioxide, and not all of the stoichiometric coefficients are integral. This time the values of $[h^0(25) - h^0(0)]$ have mostly been calculated using the modified Wilhoit-Harmens formulation^[12], as formerly implemented in the computer package GasVLe[®].

Stoichiometric equation - $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$

	$t=15\text{ }^\circ\text{C}$	$t=25\text{ }^\circ\text{C}$	$h^0(25) - h^0(15)$ [ref]	ν_i	$\nu_i [h^0(25) - h^0(15)]$
$-\text{Hc}^0(25)$	-890,58				
$i=1(\text{CH}_4)$			0,355 [7]	+1	+0,355
$i=2(\text{O}_2)$			0,293 [7]	+2	+0,586
$i=3(\text{CO}_2)$			0,369 [7]	-1	-0,369
$i=4(\text{H}_2\text{O, liquid})$			0,753 [7]	-2	-1,506
$-\text{Hc}^0(15)$	-891,51				

all values in kJ/mol

Figure 1 — Conversion of the enthalpy of combustion of the ideal gas from 25 °C to 15 °C — Methane

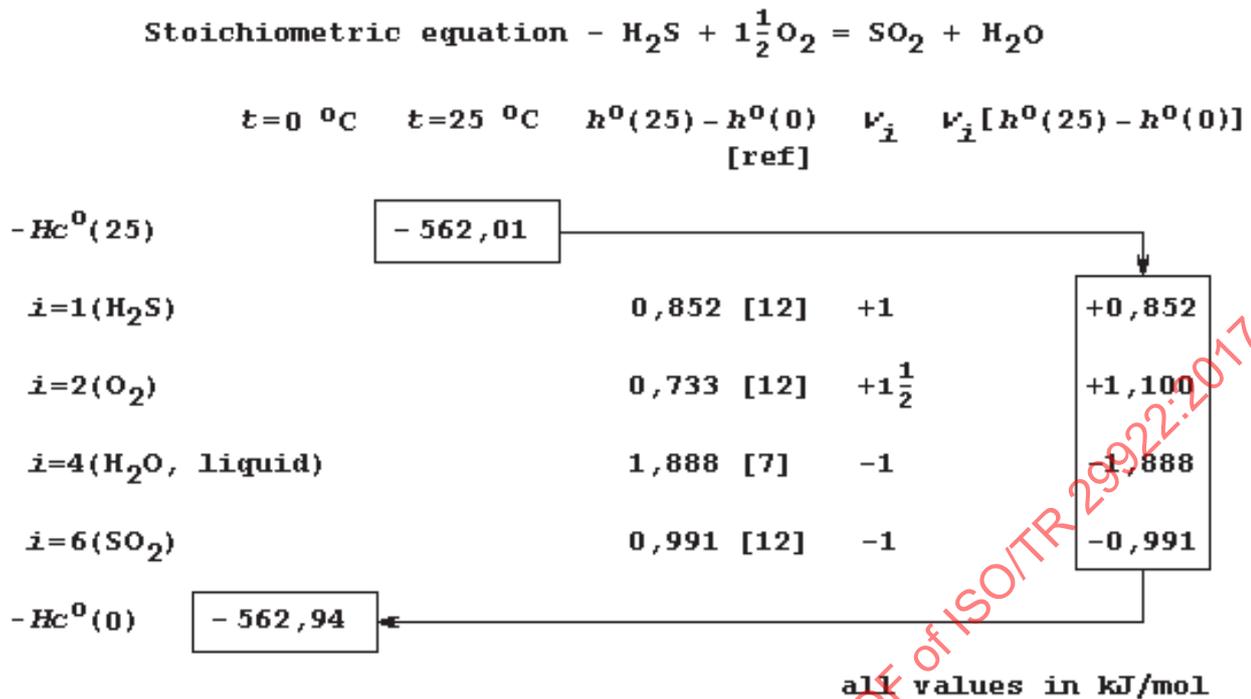


Figure 2 — Conversion of the enthalpy of combustion of the ideal gas from 25 °C to 0 °C — Hydrogen sulfide

5.6 Uncertainty in enthalpy of combustion

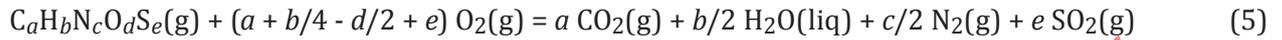
The final (right-most) column of ISO 6976:2016, Table 3 lists values for the standard uncertainty $u(Hc^0)$ in the standard enthalpy of combustion, or gross (superior) calorific value, for each of the molecular species considered in the standard. These values properly refer, in the first instance, to the standard uncertainty in the standard enthalpy of combustion at 25 °C, but they may also be applied to the standard enthalpy of combustion at each of the other reference temperatures with no loss of fitness-for-purpose.

A range of sources and techniques has been used in the derivation of the values listed, as follows:

- For methane, see 11.14.
- For ethane, propane, all isomers of butane (2), pentane (3) and hexane (5), ethene, propene, ethyne, cyclopentane, cyclohexane and benzene, the values are taken without change [except for division by 2 to convert from expanded uncertainty $U(Hc^0)$ to standard uncertainty $u(Hc^0)$] from the Table A7g column 7 of Armstrong and Jobe[7].
- For hydrogen, the standard uncertainty $u(Hc^0)$ in the standard enthalpy of combustion is taken as half of the expanded uncertainty $U(Hf^0)$ of the standard enthalpy of formation of water as reported by Rossini[19].
- For carbon monoxide, the standard uncertainty $u(Hc^0)$ is taken as half the value of $U(Hc^0)$ as reported by Rossini[20].
- For water, the value of $u(Hc^0)$ is taken as equal to the value of $u(L^0)$ given in ISO 6976:2016, A.4 which, in turn, originates from the work of Wagner and Pruss[3].

- f) For n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, the isomers of butene (4), 1-pentene, propadiene, 1,2 and 1,3-butadiene, methylcyclopentane, ethylcyclopentane, methylcyclohexane, ethylcyclohexane, toluene, ethylbenzene, o-xylene, methanol, methanethiol, carbonyl sulfide and carbon disulfide, the values of $u(Hc^o)$ were calculated from the values of expanded uncertainty $U(Hf^o)$ in the standard enthalpy of formation of the gas phase as given in Cox and Pilcher[21], as follows:

For the combustion reaction



the standard uncertainty $u(Hc^o)$ in Hc^o may be estimated by combining in quadrature the uncertainties $u(Hf^o)$ in the standard enthalpies of formation of all the reactants and products of combustion, weighted according to their stoichiometric coefficients.

Since $U(Hf^o)_{O_2} = U(Hf^o)_{N_2} = 0$, this reduces to

$$u(Hc^o) = 0,5 \times \{ [U(Hf^o)_{CHNOS}]^2 + [a \cdot U(Hf^o)_{CO_2}]^2 + [(b/2) \cdot U(Hf^o)_{H_2O}]^2 + [e \cdot U(Hf^o)_{SO_2}]^2 \}^{1/2} \quad (6)$$

where

$$U(Hf^o)_{CO_2} = 0,13 \text{ kJ} \cdot \text{mol}^{-1} \text{ (Reference [7])}$$

$$U(Hf^o)_{H_2O} = 0,042 \text{ kJ} \cdot \text{mol}^{-1} \text{ (Reference [7]), and}$$

$$U(Hf^o)_{SO_2} = 0,20 \text{ kJ} \cdot \text{mol}^{-1} \text{ (Reference [22]).}$$

The method is essentially a simple extension of the method described in Reference [7], Annex 7.

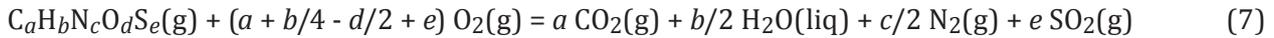
- g) For n-tridecane, n-tetradecane, n-pentadecane, hydrogen sulfide and ammonia, the method used is the same as described in (f), but in these cases values of $U(Hf^o)$ were taken from the NIST web-book[21].
- h) For the one remaining species, hydrogen cyanide, no value of either $U(Hc^o)$ or $U(Hf^o)$ appears to be available in the published literature, except for one value for $U(Hf^o)$ that seems improbably large[23]. Instead of adopting this, $U(Hf^o)$ has in this case been roughly re-estimated as the half-width of the spread of values of Hf^o reported in a selection of other published sources[4][22][24][25].

6 Non-ideality: Variation of real-gas enthalpy of combustion with pressure

6.1 Preamble

The ideal-gas molar gross calorific value $(Hc)_G^o$ of the molecular species $C_aH_bN_cO_dS_e$, where a to e are small non-negative integers is, by definition and in accordance with orthodox thermodynamic

terminology, the negative of the standard enthalpy of combustion of the combustion reaction [Formula (1)], repeated below for convenience for that species:



The definition relates formally and specifically to the hypothetical ideal reaction; that is, not only is the combustible species assumed to be in the ideal-gas state, but so too are the reactant oxygen and all of the products of combustion (except liquid water). In order, therefore, to calculate the real-gas gross calorific value $(Hc)_G$, a correction to the standard enthalpy of combustion is in principle needed to account for the fact that combustion reactions cannot in practical reality take place with all species in the ideal-gas state, but instead take place not only at a specific temperature t_1 (the combustion reference temperature) but also at a specific pressure p_1 (the combustion reference pressure).

It is convenient, if neither customary nor conventional, to use the shorthand term 'enthalpic correction' for the quantity $[(Hc)_G - (Hc)_G^o]$, where $(Hc)_G$ is the real-gas molar gross calorific value at the combustion reference temperature and pressure.

No enthalpic correction has ever in the past been included in the methodology used in any national or international standard applied to the calculation of calorific value – or, to be more precise, it has always (when considered at all) been set deliberately to zero.

6.2 Formulation of the enthalpic correction

For an individual combustible component j , the enthalpic correction to the molar enthalpy of combustion may be written as

$$[(Hc)_G - (Hc)_G^o]_j = \sum_i v_i \times [h(T, p) - h^o(T)]_i \quad (8)$$

where

- v_i is the stoichiometric coefficient of the i -th species involved in the combustion reaction, taken as positive for reactants and negative for products,
- $(h - h^o)_i$ is the molar enthalpy departure (residual enthalpy) for the i -th species involved in the combustion reaction,
- T is the temperature (the combustion reference temperature T_1 with the subscript omitted for clarity) at which the real-gas reaction takes place,
- p is the pressure (the combustion reference pressure p_1 with the subscript likewise omitted for clarity) at which the real-gas reaction takes place,

and the summation is carried out over all reactant and product species involved in the combustion reaction. This equation assumes ideal mixing, both of the reactant species and of the product species i.e. that the enthalpy of mixing is zero in each case.

For convenience (and so as to correspond with the formulation used in 5.3), we may set

- a) $i = 1$ for the combusted species j , from which it follows that $v_1 = 1$ for all j ,
- b) $i = 2$ for the reactant oxygen, whence $v_2 = [a+(b/4)-(d/2)+e]$,
- c) $i = 3$ for the product carbon dioxide, whence $v_3 = -a$,
- d) $i = 4$ for the product water, whence $v_4 = -b/2$,
- e) $i = 5$ for any product nitrogen, whence $v_5 = -c/2$, and
- f) $i = 6$ for any product sulfur dioxide, whence $v_6 = -e$.

Note that the combusted species and reactant oxygen are to be taken as initially separate and each at the reference pressure p , but that gaseous products of reaction, carbon dioxide plus any nitrogen and/or sulfur dioxide, are to be taken as a homogeneous mixture at the pressure p . However, the need for this subtle distinction disappears if ideal mixing is again invoked.

Values of the departure per mole $[h(T,p) - h^o(T)]_i$ of the actual enthalpy from the value $h^o(T)$ in the ideal-gas state at the same temperature, may be calculated if a suitable equation of state is available. For the binary molecular collision (low pressure) approximation, it can be shown^[Z] that for each reactant or product the enthalpy departure is given by

$$\frac{[h(T,p) - h^o(T)]_i}{R \cdot T} = \frac{B_i(T) - \left(T \cdot \frac{dB_i}{dT} \right)}{V_i(T,p)} \quad (9)$$

where

$B_i(T)$ is the second virial coefficient;

$V_i(T,p)$ is the molar volume, obtainable as the positive solution of the quadratic equation;

$$V_i(T,p) = (R \cdot T / p) \times [1 + B_i(T) / V_i(T,p)] \quad (10)$$

The total enthalpy departure for the whole reaction is then given by

$$[(Hc)_G - (Hc)_G^o]_j = R \cdot T \times \sum_i v_i \cdot \frac{B_i(T) - \left(T \cdot \frac{dB_i}{dT} \right)}{V_i(T,p)} \quad (11)$$

where the summation is over all six species present in the combustion reaction [Formula (7)], but with the three (possible) gaseous product species taken to be mixed homogeneously.

For a natural gas mixture, the overall combustion process may be represented as the sum of several equations of the form of Formula (7), each having a different set of values for the integers a to e and each weighted in accordance with the mole fraction of the component defined by these integers. Thus we may write

$$[(Hc)_G - (Hc)_G^o] = R \cdot T \times \sum_{j=1}^N x_j \times \sum_i v_i \cdot \frac{B_i(T) - \left(T \cdot \frac{dB_i}{dT} \right)}{V_i(T,p)} \quad (12)$$

where the inner summation is taken as before over all six reactants and products of the combustion reaction, and the outer summation is taken over all N components in the fuel gas mixture.

To make calculations of this sort is not impossible, but it is not a trivial task, largely because of the data requirements for the general evaluation of B_i and its temperature derivative. Given the complexity of calculation involved, it is therefore reassuring to note that sample calculations^[Z] using Formula (12) for natural gas type mixtures at the conditions of interest, long ago demonstrated that the total enthalpic correction is, in general, negligibly small, typically being no greater than $50 \text{ J} \cdot \text{mol}^{-1}$ (approximately 0,005 % of the enthalpy of combustion of a typical natural gas).

More specifically, it is relatively easy, using Formula (8) directly with data given in^[Z], to show (by manual calculation) that for methane $[(Hc)_G - (Hc)_G^o]$ is about $10 \text{ J} \cdot \text{mol}^{-1}$, the calorific value of the real gas being this trivial amount higher than that of the hypothetical ideal gas^[26].

For the higher hydrocarbons the enthalpic correction is in the opposite sense to that for methane, and becomes increasingly so with increasing carbon number^{[5][26]}. Given that the higher hydrocarbons are present in natural gases in steadily decreasing amounts, this observation suggests that these opposing effects might combine in order to reduce the overall enthalpic correction to very close to zero for a very wide range of natural gases.

In order to test this hypothesis, it has been thought worthwhile to revisit this kind of calculation with a more modern approach. This test might also show whether any kind of simple correction to the overall calculation procedure for calorific value is possible. One such possibility could perhaps be the application of a small constant enthalpic correction for all reasonable compositions of natural gas.

6.3 Estimation of the enthalpic correction

The modern practical approach to calculations of this sort is to employ one of the several commercially available computer program thermodynamics packages, such as GasVLe[®] or NIST-RefProp^{®2)}, which implement complex modern equations of state, and may be used to estimate values of $[h(T, p) - h^o(T)]$ directly.

NOTE Other modern (but less complex) equations of state, for example, Gibbons-Laughton (LRS) or Peng-Robinson, can be shown to generate essentially the same results in this application.

Using such a proprietary thermodynamic package, the value of $[h(T, p) - h^o(T)]_i$ of the residual enthalpy was first calculated for oxygen, nitrogen, carbon dioxide, and the first five normal alkanes using the AGA-8 equation as specified in ISO 20765-1:2005^[17].

A set of 50 thousand gas mixture compositions was then generated using a Monte Carlo (randomization) package, and the value of the enthalpic correction calculated from

$$[(Hc)_G - (Hc)_G^o] = \sum_{j=1}^N x_j \times \sum_i v_i \cdot [h(T, p) - h^o(T)]_i \tag{13}$$

for each of the 50 thousand combustion equations. The composition data were generated using the following composition-limit rules:

	lower limit	upper limit
mole fraction N ₂	0,000	0,035
mole fraction CO ₂	0,000	0,020
mole fraction C ₂ H ₆	0,000	0,050
mole fraction C ₃ H ₈	0,000	0,020
mole fraction C ₄ H ₁₀	0,000	0,005
mole fraction C ₅ H ₁₂	0,000	0,002
mole fraction CH ₄	0,800	1,000
		(calculated by difference)

with, in all cases, C₂ > C₃ > C₄ > C₅.

The results for $[(Hc)_G - (Hc)_G^o]$ (including one standard deviation) are as follows:

2) GasVLe[®] and NIST-RefProp[®] are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

- at $T = 298,15 \text{ K}$ $[(Hc)_G - (Hc)_G^o] = (0,010 \pm 0,001) \text{ kJ}\cdot\text{mol}^{-1}$
- at $T = 288,15 \text{ K}$ $[(Hc)_G - (Hc)_G^o] = (0,011 \pm 0,001) \text{ kJ}\cdot\text{mol}^{-1}$
- at $T = 273,15 \text{ K}$ $[(Hc)_G - (Hc)_G^o] = (0,013 \pm 0,001) \text{ kJ}\cdot\text{mol}^{-1}$

6.4 Conclusion

As noted earlier, values of the enthalpic correction are tiny when compared to the enthalpy of combustion values that they may be used to “adjust” or “correct”; indeed, they are substantially smaller even than the estimated uncertainty of the enthalpy of combustion of methane (see 11.1.4). A typical natural gas has a standard enthalpy of combustion of about $1\,000 \text{ kJ}\cdot\text{mol}^{-1}$, quoted invariably (as are the enthalpies of combustion of its components) to no more than two decimal places and with an uncertainty of no better (and possibly much worse) than about $0,20 \text{ kJ}\cdot\text{mol}^{-1}$. When considered in the context of these figures the value of $[(Hc)_G - (Hc)_G^o]$ calculated in 6.3 might simply and justifiably be rounded to

$$[(Hc)_G - (Hc)_G^o] = + (0,01 \pm 0,00) \text{ kJ}\cdot\text{mol}^{-1}$$

and used as a constant correction in all relevant calculations.

However, and despite the observations

- a) that to omit this correction not only misses an opportunity to improve the thermodynamic respectability of ISO 6976, but
- b) its omission also introduces (or, to be more precise, retains) a tiny known bias into the calculation of real-gas calorific value, and
- c) that its inclusion would be essentially correct and present no sensible increase in complexity of any calculation prescribed in ISO 6976.

it is nevertheless clear that to include this correction also offers no discernible numerical improvement.

For this reason, corrections for the difference in enthalpy of combustion between the ideal gas and the real gas, and for variation of real-gas enthalpy of combustion with pressure, are not applied in the calculation procedures prescribed in ISO 6976.

7 Non-ideality: Compression factor effect on volume-basis calorific values

7.1 Compression factor

The volume $V(\text{ideal})$ occupied, at the metering reference conditions (T_2, p_2) , by one mole of a gas which behaves in accordance with the so-called ideal gas law (see ISO 6976:2016, 3.8) is given by

$$V(\text{ideal}) = R \cdot T_2 / p_2 \quad (14)$$

where T_2 is the absolute (kelvin) temperature corresponding to the Celsius temperature t_2 .

No actual gas, and certainly no real natural gas, precisely obeys the ideal gas law. Accordingly, the volume $V(\text{real})$ occupied by one mole of a real gas is often related to $V(\text{ideal})$ through use of the quantity Z , known as the compression factor, such that

$$V(\text{real}) = Z(T_2, p_2) \cdot V(\text{ideal}) \quad (15)$$

$$= Z(T_2, p_2) \cdot R \cdot T_2 / p_2 \quad (16)$$

Compression factor is generally a function of temperature, pressure and gas composition; it may be greater than or (more often) less than unity, but is usually close to unity for “permanent” gaseous substances.

The effect of compression factor on volume-basis calorific value is straightforward. The smaller Z , the smaller [Formula (15)] is the volume that contains one mole (i.e. unit amount of substance) of the real gas; and, therefore, the greater, in inverse proportion, is the amount of any extensive quantity, such as enthalpy of combustion (or calorific value) per unit volume. Accordingly (and ignoring second order effects that are considered and deemed negligible in Clause 6), we have

$$Hv(\text{real}) = Hv(\text{ideal}) / Z \quad (17)$$

Or, using the symbols more generally adopted elsewhere throughout ISO 6976 and this document

$$Hv = (Hv)^o / Z \quad (18)$$

7.2 Virial equation of state

The theory of statistical mechanics provides both an insight to the general dependence of compression factor Z on temperature, pressure and composition, and a means for its evaluation, for a mixture of arbitrary composition, from the known properties of the components of the mixture.

The basic statistical mechanical expression for Z is an infinite series of the following form:

$$Z(T, p) = p \cdot V / R \cdot T \quad (19)$$

$$= 1 + B(T) / V + C(T) / V^2 + \dots J(T) / V^{j-1} + \dots \quad (20)$$

where $V(\text{real})$, the molar volume, has been abbreviated to V for clarity. The molar volume V is the reciprocal of the molar density D .

In this expression, the quantities $B(T)$, $C(T)$, ... $J(T)$ are known as the second, third, ... j -th virial coefficients respectively. Each is a function of temperature and composition, but is independent of pressure. The term containing the second virial coefficient accounts for the effect upon Z of two-body molecular interactions (both like-molecule and unlike-molecule); likewise the term containing the third virial coefficient accounts solely for the effects of three-body molecular interactions, and so on. At the pressures of interest in ISO 6976, three-body and higher order interactions are relatively rare; hence the virial expansion may be truncated at the second term, with no significant loss of accuracy. Thus

$$Z = Z(T, p) = 1 + [B(T) / V] \quad (21)$$

$$= 1 + p \cdot B(T) / Z(T, p) \cdot R \cdot T \quad (22)$$

which may be solved as a quadratic in Z if B is known. All the above is applicable to pure gases and mixtures alike.

Statistical mechanics also provides an expression for B for a multicomponent mixture of arbitrary composition as follows:

$$B(T) = \sum_j^N \sum_k^N x_j \cdot x_k \cdot B_{jk}(T) \quad (23)$$

$$\text{with } B_{jk}(T) = B_{kj}(T) \quad (24)$$

and where each summation is taken over all N components of the mixture. In this expression, there are N like-interaction (pure component) terms of the form $x_j^2 \cdot B_{jj}$ and $N \cdot (N-1)/2$ unlike (mixed) interaction terms of the form $2x_j \cdot x_k \cdot B_{jk}$.

It is not practicable to provide numerical values for all B_{jj} and all B_{jk} for each of the metering reference temperatures T_2 of interest; this would require some 7320 values (see Note), a rather high proportion of which would have to be based on some estimative or correlative technique.

NOTE This value is calculated as $4 \times [N + N \cdot (N-1)/2]$ for $N = 60$, there being four commonly used values for T_2 .

Clearly, then, a substantial reduction of the data requirement in accordance with a well-understood (and well-behaved) specific approximation is necessary if $Z(T, p)$, and hence $V(\text{real})$, are to be readily calculable from [Formulae \(22\)](#) and [\(16\)](#). This is especially so if the method is required to be amenable to hand calculation as well as machine computation.

7.3 Estimation of mixture compression factor

One specific approximation scheme for the estimation of Z , recommended by some respected authorities^[2], is to retain only the N like-interaction terms and the $(N-1)$ unlike-interaction terms involving methane as one component (i.e. terms of the form $2x_1 \cdot x_k \cdot B_{1k}$, where the subscript 1 refers to methane). This formulation has the merit of severely reducing the number of terms to be evaluated (but only to 476), and the virial coefficients in those terms that remain are in many cases, but by no means all, reasonably accessible; moreover, the terms omitted (i.e. all other $2x_j \cdot x_k \cdot B_{jk}$ terms for $j, k \neq 1$) can, not unreasonably, be treated as negligible in any calculation where $x_j, x_k \ll x_1$ for all j, k , as is often, but not invariably, the case for natural gas.

However, for the purposes of ISO 6976, an alternative simplification scheme, dating in essence from a report (IGT-32) published long ago^[27] by the Institute of Gas Technology, has been preferred that has the advantage of retaining *all* terms, the like-interaction terms being correctly represented and the unlike-interaction terms being represented in accordance with a specific approximation.

The simplification involved may be understood by taking the truncated virial [Formula \(22\)](#) with the compression factor $Z(T, p)$ omitted from the right-hand side (or, to be more precise, substituted by unity), as follows:

$$Z(T, p) = 1 + p \cdot [B(T) / R \cdot T] \quad (25)$$

This commonly used approximation has the effect of converting a quadratic equation in Z into a linear equation.

Combining [Formula \(25\)](#) with [Formula \(23\)](#) results in

$$Z = 1 + \frac{p}{R \cdot T} \sum_j^N \sum_k^N (x_j \cdot x_k) \times B_{jk} \quad (26)$$

By allowing the further approximation of

$$B_{jk} \approx \sqrt{B_{jj} \cdot B_{kk}} \quad (27)$$

for all j, k , we then have

$$Z(T, p) = 1 + \frac{p}{R \cdot T} \sum_j^N \sum_k^N (x_j \cdot x_k) \times \sqrt{B_{jj} \cdot B_{kk}} \quad (28)$$

Although [Formula \(27\)](#) has no formal basis in statistical mechanics, this geometric-mean approximation is usually reasonably accurate for mixtures composed of molecules which are not too dissimilar in size, shape and polarity.

[Formula \(28\)](#) may clearly be rewritten as

$$Z(T, p) = 1 - \sum_j^N \sum_k^N (x_j \cdot x_k) \times \sqrt{\left[-B_{jj} \cdot \left(\frac{p}{R \cdot T} \right) \right] \times \left[-B_{kk} \cdot \left(\frac{p}{R \cdot T} \right) \right]} \quad (29)$$

or

$$Z(T, p) = 1 - \sum_j^N \sum_k^N (x_j \cdot x_k) \times \left[s_j(T, p) \cdot s_k(T, p) \right] \quad (30)$$

in which the quantity s_j is usually referred to as the summation factor and is defined by

$$s_j(T, p) = \sqrt{\left[-B_{jj}(T) \cdot \left(\frac{p}{R \cdot T} \right) \right]} \quad (31)$$

which (in the present approximation) may also be written as

$$s_j(T, p) = \sqrt{1 - Z_j(T, p)} \quad (32)$$

The double summation in [Formula \(30\)](#) can be shown to reduce as an exact mathematical identity to a single summation, as follows:

$$Z(T, p) = 1 - \left[\sum_{j=1}^N x_j \times s_j(T, p) \right]^2 \quad (33)$$

which forms the basis of the compression factor calculation procedure implemented in the superseded ISO 6976:1995. In that standard the summation factors were in general calculated from compression factor data [[Formula \(32\)](#)], often a hypothetical gas-phase value, whereas in the third edition they are in general calculated directly from second virial coefficient data [[Formula \(31\)](#)].

That procedure is, however, slightly amended in another way for ISO 6976:2016, as follows. By applying [Formula \(31\)](#) to two different pressures p_2 and p_0 , it is straightforward to rewrite [Formula \(33\)](#) as

$$Z(T_2, p_2) = 1 - \left(\frac{p_2}{p_0} \right) \times \left[\sum_{j=1}^N x_j \times s_j(T_2, p_0) \right]^2 \quad (34)$$

where p_0 is a reference pressure, taken always in this context as 101,325 kPa, and the subscript 2 refers to the metering reference conditions. The quantity

$$s(T_2, p_0) = \sum_{j=1}^N x_j \times s_j(T_2, p_0) \quad (35)$$

may self-evidently be identified as the summation factor for the complete mixture.

Thus the compression factor $Z(T_2, p_2)$ at any metering reference pressure p_2 may be calculated simply from known values of the summation factor at the reference pressure p_0 . This equation is used as the basis of all compression factor calculations in ISO 6976:2016.

It is a convenient shorthand to refer to the overall procedure as the (much) modified (or modernised) IGT-32 method. [Formula \(34\)](#) retains *all* the terms in the original double-summation formulation for $Z(T, p)$, as expressed by [Formulae \(22\)](#) and [\(23\)](#), but uses only the values of the pure component second virial coefficients $B_{jj}(T)$ to do so.

7.4 Limitations of the modified IGT-32 method

[Formula \(34\)](#) cannot be used uncritically. In addition to uncertainties in compression factor Z that arise directly from uncertainties in pure-component second virial coefficients, there are three other sources of uncertainty, which may result in bias or systematic error in the method, as follows:

- truncation of the virial expansion at the two-body interaction (second virial coefficient) term, thereby ignoring the higher order interaction terms [[Formula \(21\)](#)],
- linearization of the truncated virial equation [[Formula \(25\)](#)], and
- expression of an interaction second virial coefficient B_{jk} as the geometric mean of the two pure-component second virial coefficients B_{jj} and B_{kk} [[Formula \(27\)](#)].

At the ambient pressures of interest in the present context, and for natural gases that are very close to ideality, the factors a) and b) may be anticipated as of only minor significance. Nonetheless, a purposeful numerical analysis of the effects of these factors is needed in order to avoid the uncritical and inappropriate application of the method to gases that are not sufficiently close to ideality.

Such an analysis is given in [8.4.2](#) and [8.4.3](#). One conclusion is that the method should not be used for mixtures where the calculated value of compression factor is less than 0,90. At this limiting value, the bias error is in general about 2 %. To keep the bias below 0,1 % the lower limit value of compression factor should be about 0,97.

The effects of factor c) need also to be critically addressed. First, there is the general issue of how well interaction second virial coefficients are represented by the geometric mean of the pure component second virial coefficients, but second, there are well-known specific cases where this approximation cannot, even in principle, work at all, and therefore require specific resolution.

These latter cases are those for which the second virial coefficient of one of the interacting pair is positive (corresponding to a compression factor of greater than unity) and for the other, as is more normally the case, is negative. The geometric mean of the component second virial coefficients is therefore an imaginary quantity. The most common examples of gases for which the compression factor is greater than unity at ambient conditions are hydrogen, helium and neon. For the interaction of any of these with the commoner components of natural gas, therefore, the geometric mean approximation not only fails but gives an impossible result.

Corresponding exactly to this situation, the summation factors for hydrogen, helium and neon, if derived directly from the defining [Formula \(31\)](#), are imaginary – as such they have no physical meaning and cannot be used in [Formula \(34\)](#).

The resolution of this issue is discussed further in [8.2](#). Suffice to say here that the special treatment needed to avoid this problem involves, in these cases, abandoning the defining [Formula \(31\)](#) and instead selecting numerically acceptable “real” pseudo-values for the summation factors, good enough for the purposes of ISO 6976:2016 and allowing [Formula \(34\)](#) to be used without formal change, but including an allowance for an extra contribution to the overall uncertainty of calculation from this source.

7.5 Uncertainty in compression factor

There are (at least) two strategies available to take into account the uncertainties involved in applying [Formula \(34\)](#) to the calculation of compression factor.

One is to rewrite [Formula \(34\)](#) with an additive correction term ζ as

$$Z(T_2, p_2) = 1 + \zeta - \left(\frac{p_2}{p_0} \right) \times \left[\sum_{j=1}^N x_j \times s_j(T_2, p_0) \right]^2 \quad (36)$$

where $\zeta = 0$ but with a standard uncertainty $u(\zeta) > 0$. The value of $u(\zeta)$ would then be combined in quadrature with the standard uncertainty $u(s)$ of the mixture summation factor $s(T_2, p_0)$, as calculated from the standard uncertainties $u(x_j)$ and $u(s_j)$ of the component mole fractions x_j and summation factors s_j respectively, so as to calculate the standard uncertainty $u(Z)$ in the mixture compression factor Z . Of course the question of how to estimate $u(\zeta)$ is the critical issue in this strategy. This approach has not been adopted for use in ISO 6976.

The preferred alternative strategy is to subsume all of the uncertainties, from all the sources as identified in [7.4](#), into an overall uncertainty in each of the component summation factors. How this procedure is carried out is elaborated more fully in [Clause 8](#), in particular in [8.5](#). What it means in practice, however, is that the uncertainties attributed to the summation factors are significantly greater than those that result from the known uncertainties in the second virial coefficients from which the summation factors are calculated.

8 Quantitation of volumetric non-ideality

8.1 Second virial coefficients of pure components

8.1.1 Preliminary procedures

As explained in [Clause 7](#), the starting point for expressing the volumetric non-ideality of a natural gas or similar mixture is a set of values for the second virial coefficients $B(T_2)$ for the individual pure components of the mixture at each of the relevant metering reference temperatures T_2 .

The initial procedure adopted was to select what appear to be the best open-literature sources (including reviews) of relevant values at temperatures within (or, failing that, reasonably close to) the range of temperatures required.

For the majority of components (48 out of 60), the chosen source of the best values (i.e. the most recent and most reputable expert evaluation) is the Landolt-Börnstein compilation[28], itself an update of the previously published classic text on the topic[29]. For each component, this source lists experimental measurements of B , a recommended fourth-order polynomial in reciprocal temperature (used for interpolation where necessary and, in a few instances, for judicious extrapolation) and an estimated uncertainty.

For the remaining 12 components not covered by the Landolt-Börnstein compilation, namely the normal alkanes n-nonane to n-pentadecane, 1,2-butadiene, ethylcyclopentane, methylcyclohexane,

ethylcyclohexane and methyl mercaptan, values were derived using the Tsonopoulos extension^[30] to the Pitzer-Curl Formula^[31], as follows:

$$\frac{B(T) \cdot p_c}{R \cdot T_c} = (0,1445 + 0,0637 \cdot \omega) - \frac{0,330}{T_r} - \frac{(0,1385 - 0,331 \cdot \omega)}{T_r^2} - \frac{(0,0121 + 0,423 \cdot \omega)}{T_r^3} - \frac{(0,000607 + 0,008 \cdot \omega)}{T_r^8} - \frac{(2,140 \times 10^{-4} \cdot \mu_r + 4,308 \times 10^{-21} \cdot \mu_r^8)}{T_r^6} \quad (37)$$

where the reduced dipole moment μ_r is given by

$$\mu_r = (10^5 \cdot \mu^2) \times \frac{p_c}{T_c^2} \quad (38)$$

Values of the parameters needed as input to the Tsonopoulos equation, namely critical temperature T_c and pressure p_c , acentric factor ω and dipole moment μ were taken in the first instance from the well-known classic text of Poling, Prausnitz and O'Connell^[32] or, if not present in that source, from Reid, Prausnitz and Poling^[33].

By using the above procedures, it was possible to generate a set of second virial coefficient $B(T_2)$ values from which, in turn, a set of summation factors could be derived using [Formula \(31\)](#) that would satisfactorily serve the purposes of ISO 6976. These procedures represent a sensible, albeit minor, improvement over the methods used for generating the corresponding compression factor (or hypothetical compression factor) values listed in ISO 6976:1995.

8.1.2 Improved procedure

However, it later became apparent that an even (very slightly) better (i.e. more 'tuned' to the present application) set of second virial coefficient values could be generated for all of the major and most of the minor components (43 of 60 in total) of a typical natural gas by use of the 'reference quality' (or in some cases almost reference quality) equations of state that have more recently become available. These complex (so-called fundamental) equations have been carefully evaluated and implemented in the NIST-RefProp[®] thermodynamic properties computer package^[34] that can be used to generate compression factor and/or second virial coefficients directly.

In brief the improved procedure adopted was as follows. Best-estimate compression factor data were generated for each fluid using RefProp in the range 250 to 350 K and at 101,325 kPa (1 atm) pressure (or at the saturation vapour pressure for those fluids not in the gaseous state at 1 atm). The values so generated were then used with [Formula \(25\)](#) so as to obtain values of the second virial coefficient B within the temperature range defined above. The four metering reference temperatures to which ISO 6976 is applicable are all close to the middle of this range.

These values of B for each fluid were then fitted to a dimensionless equation of the form

$$B \cdot p_2 / R \cdot T = g_1 \cdot \tau + g_2 \cdot \tau^{1,2} + g_3 \cdot \tau^{g_4} \quad (39)$$

where $\tau = 100 \text{ K}/T$ and $p_2 = 101,325 \text{ kPa}$.

The best-fit dimensionless parameters g_1 to g_4 for each fluid were then used to provide definitive interpolated values of B at each of the four metering reference temperatures T_2 ($= t_2 + 273,15 \text{ K}$) considered in ISO 6976. From these values, it is straightforward, using [Formula \(31\)](#), to generate the required values of $s(t_2, p_0)$ and (where the fluid is gaseous at t_2), using [Formula \(25\)](#) to generate values of the compression factor $Z(t_2, p_0)$.

As noted previously, this treatment is only available for 43 of the 60 fluids listed in ISO 6976. For 14 of the remaining 17 fluids, the values obtained from the methods outlined in 8.1.1 were retained. For the special cases of hydrogen, helium and neon, see 8.2.3.

Table 1 provides a list of the sources of the data used in these derivations.

Table 1 — Data sources used in the estimation of summation factors

<i>j</i>	Component	Source reference(s)
1	methane	[36][44]
2	ethane	[37]
3	propane	[38]
4	n-butane	[47]
5	2-methylpropane	[47]
6	n-pentane	[97]
7	2-methylbutane	[41]
8	2,2-dimethylpropane	[41]
9	n-hexane	[97]
10	2-methylpentane	[41]
11	3-methylpentane	method of 8.1.1
12	2,2-dimethylbutane	method of 8.1.1
13	2,3-dimethylbutane	method of 8.1.1
14	n-heptane	[97]
15	n-octane	[97]
16	n-nonane	[41]
17	n-decane	[41]
56	n-undecane	[98]
57	n-dodecane	[99]
58	n-tridecane	unpublished
59	n-tetradecane	unpublished
60	n-pentadecane	unpublished
18	ethene	[48]
19	propene	[52]
20	1-butene	[100]
21	cis-2-butene	[100]
22	trans-2-butene	[100]
23	2-methylpropene	[100]
24	1-pentene	method of 8.1.1
25	propadiene	method of 8.1.1
26	1,2-butadiene	method of 8.1.1
27	1,3-butadiene	method of 8.1.1
28	ethyne	method of 8.1.1
29	cyclopentane	[101]
30	methylcyclopentane	method of 8.1.1
31	ethylcyclopentane	method of 8.1.1
32	cyclohexane	[102]
33	methylcyclohexane	unpublished
34	ethylcyclohexane	method of 8.1.1

Table 1 (continued)

<i>j</i>	Component	Source reference(s)
35	benzene	[103]
36	toluene	[41]
37	ethylbenzene	[104]
38	o-xylene	[104]
39	methanol	[105]
40	methanethiol	method of 8.1.1
41	hydrogen	see 8.2.3
42	water	[3]
43	hydrogen sulfide	[41]
44	ammonia	[106]
45	hydrogen cyanide	method of 8.1.1
46	carbon monoxide	[41]
47	carbonyl sulfide	[41]
48	carbon disulfide	method of 8.1.1
49	helium	see 8.2.3
50	neon	see 8.2.3
51	argon	[50]
52	nitrogen	[39]
53	oxygen	[107][108]
54	carbon dioxide	[40]
55	sulfur dioxide	[41]

8.2 Summation factors of pure components

8.2.1 Overview

For each component fluid (except for hydrogen, helium and neon) the second virial coefficients $B(T_2)$ derived, for each metering reference temperature, from the procedures summarized in 8.1 were converted into summation factors $s(t_2, p_0)$ by use of the defining Formula (31). The resulting values are those given in ISO 6976:2016, Table 2.

8.2.2 Major components of natural gas

It is interesting to compare summation factors derived as described above with those calculated from various high-quality equations of state. Table 2 provides such a comparison for $t_2 = 15$ °C for the more important components of a typical natural gas, namely methane, ethane, propane, nitrogen and carbon dioxide, plus carbon monoxide. In this table, the methods employed (in listed order) are as follows:

- values as calculated by the method of 8.1.2 and taken directly from ISO 6976:2016, Table 2;
- values as calculated by the method of 8.1.1;
- values given in ISO 6976:1995;
- values derived, via Formula (31), from values of second virial coefficient calculated using the MGERG formulation as presented in GERG TM-2[35];
- values derived from values of second virial coefficient calculated directly using the default equations in NIST-RefProp[34] – methane[36], ethane[37], propane[38], nitrogen[39], carbon dioxide[40], carbon monoxide[41];

- f) values derived, via [Formula \(32\)](#), from values of compression factor calculated using the MGERG equation[35];
- g) values derived from values of compression factor calculated using the AGA-8-92DC equation[17][42];
- h) values derived from values of compression factor calculated using the GERG-2004 equation as presented in GERG TM-15[43];
- i) values derived from values of compression factor calculated using the modified Benedict-Webb-Rubin (MBWR) equation of state – methane[44], ethane[37], propane[45], nitrogen[39], carbon dioxide[40], carbon monoxide[41];
- j) values derived from values of compression factor calculated using default equations in NIST-RefProp [same source documentation as (e)].

Table 2 — Values of summation factor for major gases at 15 °C and 101,325 kPa calculated by various methods

Method	Methane	Ethane	Propane	Nitrogen	Carbon dioxide	Carbon monoxide
a)	0,044 52	0,091 9	0,134 4	0,017 0	0,075 2	0,021 7
b)	0,044 53	0,091 6	0,134 2	0,017 2	0,075 1	0,021 2
c)	0,044 7	0,092 2	0,133 8	0,017 3	0,074 8	0,022 4
d)	0,044 52	0,091 8	0,133 5	0,017 0	0,075 2	0,021 3
e)	0,044 53	0,091 6	0,133 3	0,017 1	0,075 0	0,021 7
f)	0,044 51	0,092 1	0,134 6	0,016 9	0,075 4	0,021 2
g)	0,044 45	0,092 1	0,134 6	0,017 1	0,075 1	0,020 8
h)	0,044 48	0,092 0	0,133 8	0,017 0	0,075 2	0,020 4
i)	0,044 52	0,091 9	0,134 5	0,017 0	0,075 2	0,021 7
j)	0,044 52	0,091 9	0,134 4	0,017 0	0,075 2	0,021 7

It seems reasonable to interpret this table as suggesting that, for the major gases at least, it makes little difference which of the calculational methods is selected to provide the values of s for ISO 6976. The differences observed between the various methods are essentially trivial.

The concordance between the methods might at first sight be thought of as providing some indication of the uncertainty $u(s)$ in s . However such an inference would hardly be valid, for it is of course the case that each of the methods uses more-or-less the same experimental PVT-data (compression factor Z and/or density D) as sources to contribute to the evaluation of the parameters of the various equations of state.

In essence, the selection of the main procedure chosen for providing the data required for ISO 6976 is largely predicated by the availability of extensive coverage of the less-common components of natural gas, thus allowing their treatment within a consistent and thorough methodology.

8.2.3 Hydrogen and helium

Because it would result in mathematically (and physically) unreal values of summation factor (see also 7.4), the methodology presented in 8.1 is not applicable to hydrogen, helium and neon (although the fitting process for B described in 8.1.2 can still be carried out satisfactorily). For these gases the summation factors listed in ISO 6976:2016, Table 2 (–0,01 in each case) have been derived by comparison of trial-and-error calculations for mixtures of methane with the component in question against more rigorous calculations made using the complex thermodynamic property calculation packages referred to elsewhere, and (see 8.4.5) an extra allowance, probably an over-estimate, has been made in the uncertainty assigned to these values.

8.3 Compression factors of the permanent gases

This subclause provides best-estimate values for the compression factor of the so-called 'permanent' (and some other) gases included in the set of components covered by ISO 6976, either taken directly from experiment, or from the fitting of high-quality PVT-data to a good interpolative equation of state, and compares these with values calculated from the values of summation factor given in ISO 6976:2016, Table 2.

The values of Z (best value) given in Table 3 for these gases have been taken from the following sources: methane[44], ethane[37], propane[46], butanes[46,47], ethene[48], neon[49], argon[50], nitrogen[39], carbon dioxide[40], most of which are collected together in Richter et al.[51] All the values refer to 0 °C and 101,325 kPa. For the other permanent gases in Table 3, the values given are reproduced (without uncertainties) from ISO 6976:1995.

The standard uncertainties $u(Z)$ for the best-value compression factors are taken from the source documentation, whereas those for the compression factors derived from summation factors (using Formula (32) in reverse) are calculated as $2s \cdot u(s)$, where the values of $u(s)$ used are those given alongside the summation factors in ISO 6976:2016, Table 2. In general the latter values of uncertainty are much greater than the former; the reasons for this are explained further in 8.4 and 8.5.

Table 3 — Comparison of compression factors for permanent gases at 0 °C and 101,325 kPa

j	Component	Compression factor Z (best value)	Standard uncertainty $u(Z)$	Compression factor $Z(s)$ from s	Standard uncertainty $u(Z(s))$
1	methane	0,997 613	0,000 008	0,997 613	0,000 049
2	ethane	0,990 052	0,000 025	0,990 060	0,000 219
3	propane	0,978 60	0,000 10	0,978 54	0,000 47
4	n-butane	0,959 1	0,000 4	0,959 1	0,001 6
5	2-methylpropane	0,964 5	0,000 2	0,964 5	0,001 2
18	ethene	0,992 468	0,000 010	0,992 466	0,000 174
19	propene	0,981		0,980 9	0,000 4
28	ethyne	0,991		0,991 2	0,000 4
41	hydrogen	1,000 6		0,999 9	0,000 5
43	hydrogen sulfide	0,990		0,989 9	0,000 5
44	ammonia	0,985		0,984 9	0,000 5
46	carbon monoxide	0,999 3		0,999 33	0,000 05
49	helium	1,000 5		0,999 9	0,000 5
50	neon	1,000 484	0,000 015	0,999 9	0,000 5
51	argon	0,999 056	0,000 005	0,999 058	0,000 061
52	nitrogen	0,999 543	0,000 005	0,999 542	0,000 043
53	oxygen	0,999 0		0,999 03	0,000 06
54	carbon dioxide	0,993 259	0,000 010	0,993 260	0,000 328
55	sulfur dioxide	0,976		0,975	0,001

Table 4 provides, for the same set of 'permanent' gases, a definitive and internally consistent set of values of compression factors (without uncertainties) determined using the thermodynamic calculation package NIST-RefProp version 9.1[34], for the four metering reference temperatures t_2 considered in ISO 6976.

To achieve consistency, this package implements *inter alia* the GERG-2004 equation of state[43], using which the values for methane, ethane, propane, n-butane, 2-methylpropane (iso-butane), hydrogen, helium, argon, nitrogen, oxygen and carbon dioxide have been computed. Other sources used by RefProp are: for ethene[48], propene[52], hydrogen sulfide, carbon monoxide and sulfur dioxide[41], ammonia[53]

and neon^[49]. All the values are for a reference pressure p_0 of 101,325 kPa. Note that the compression factor values listed are not exactly interconvertible with the summation factors given in ISO 6976, nor are the values for 0 °C identical with the 'best-value' listing in [Table 3](#). The last digit (at least) for the values given in [Table 4](#) should be considered as no more than an aid to interpolation.

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Table 4 — Compression factors for permanent gases at metering reference temperatures

<i>j</i>	Component	Compression factor $Z(t_2, p_0)$			
		$t_2 = 0\text{ °C}$	$t_2 = 15\text{ °C}$	$t_2 = 60\text{ °F}$	$t_2 = 20\text{ °C}$
1	methane	0,997 62	0,998 02	0,998 04	0,998 14
2	ethane	0,990 01	0,991 53	0,991 58	0,991 97
3	propane	0,978 70	0,982 10	0,982 21	0,983 06
4	n-butane	0,959 49	0,966 50	0,966 72	0,968 45
5	2-methylpropane	0,964 28	0,970 30	0,970 49	0,971 99
18	ethene	0,992 47	0,993 61	0,993 65	0,993 94
19	propene	0,980 94	0,983 95	0,984 05	0,984 81
41	hydrogen	1,000 61	1,000 60	1,000 60	1,000 59
43	hydrogen sulfide	0,989 89	0,991 48	0,991 53	0,991 93
44	ammonia	0,984 86	0,987 89	0,987 99	0,988 71
46	carbon monoxide	0,999 34	0,999 53	0,999 54	0,999 59
49	helium	1,000 54	1,000 51	1,000 51	1,000 50
50	neon	1,000 50	1,000 49	1,000 49	1,000 48
51	argon	0,999 04	0,999 24	0,999 24	0,999 30
52	nitrogen	0,999 55	0,999 71	0,999 72	0,999 76
53	oxygen	0,999 00	0,999 21	0,999 22	0,999 27
54	carbon dioxide	0,993 25	0,994 34	0,994 38	0,994 66
55	sulfur dioxide	0,975 09	0,980 24	0,980 40	0,981 61

8.4 Pure component uncertainties

8.4.1 Uncertainty of second virial coefficients

From [Formula \(31\)](#) it is easy to infer mathematically that the standard uncertainty $u(s_j)$ in the summation factor s_j of a pure component is given by

$$u(s_j)/s_j = u(B_{jj})/2 \cdot B_{jj} \quad (40)$$

where $u(B_{jj})$ is the standard uncertainty in the second virial coefficient B_{jj} .

However this identity is misleading because, as explained in [7.4](#), [Formula \(31\)](#) is based on the two approximations whereby [Formula \(20\)](#) is both truncated at the second term and linearized so as to become [Formula \(25\)](#).

In order to obtain true estimates of the uncertainties of the summation factors, it is in principle, therefore, necessary to take into account contributions from three sources, only the first of which is accounted for by [Formula \(40\)](#).

For this first contribution, values of $u(B_{jj})$ for most of the components considered in ISO 6976 are given in Landolt-Börnstein[28]. For those few cases where B_{jj} and $u(B_{jj})$ are not available from that source, this first component of $u(s_j)$ was set somewhat arbitrarily (but conservatively) to 0,01.

8.4.2 Truncation error

Although separate in conceptual origin, the effects on uncertainty of truncation and linearization can be combined and treated as a single issue. This may be achieved by estimating the difference between Z_j (and hence s_j) as calculated

- a) from the two-term virial expansion in pressure p [[Formula \(25\)](#)], and

- b) from the more rigorous three (or more)-term virial expansion in inverse molar volume $1/V$, or molar density, D [Formula (20)],

and setting the value so obtained as the truncation error (more correctly, the truncation bias) in $u(Z_j)$.

For the purposes of this comparison, the second virial coefficient B_{jj} may be estimated from the Tsonopoulos correlation^[30] [Formula (37)] and the third virial coefficient C_{jjj} from the correlation of Orbey and Vera^[54], as follows

$$\begin{aligned} \frac{C(T) \cdot p_c^2}{(R \cdot T_c)^2} &= (0,01407 - 0,02676 \cdot \omega) + \frac{(0,02432 + 0,01770 \cdot \omega)}{T_r^{2,8}} \\ &+ \frac{0,040 \cdot \omega}{T_r^{3,0}} - \frac{0,003 \cdot \omega}{T_r^{6,0}} - \frac{(0,00313 + 0,00228 \cdot \omega)}{T_r^{10,5}} \end{aligned} \quad (41)$$

This procedure follows that recommended in Landolt-Börnstein^[28], where it is explained in greater detail. Values of critical temperature T_c and pressure p_c and acentric factor ω required for Formula (41) were taken from the same sources as used for Formula (37)^{[32][33]}. The solution of Formula (20) for Z_j for this purpose clearly requires an iterative procedure. The second contribution to $u(s_j)$ is then estimated finally from the difference [Z_j Formula (20) - Z_j Formula (25)], where the second and third virial coefficients are estimated using Formulae (37) and (41), respectively.

For several of the heavier components required for ISO 6976 (in general those of carbon number 7 and above) this procedure cannot, however, be used. In these cases this second contribution to $u(s_j)$ was set conservatively to 0,10, approximately twice the greatest value found for other components.

The kind of analysis outlined above can also be applied in a more general, but perhaps more instructive, fashion. Instead of taking the 'known' values of T_c , p_c and ω for each individual component and carrying through the calculation, an alternative is simply to choose a range of values for each of these parameters and to carry through the calculation for each combination of these parameters so as to obtain a set of results for, in essence, a large set of 'hypothetical' components (or mixtures).

An analysis of this kind was performed as follows. The critical temperature T_c was varied from 150 K to 500 K in steps of 50 K, the critical pressure p_c varied from 1 MPa to 6 MPa in steps of 0,5 MPa, and the acentric factor varied from 0 to 0,7 in steps of 0,1. This gives a set of $8 \times 6 \times 8 = 384$ hypothetical components.

The results so obtained for the bias between Formula (20) and Formula (25) are shown as the filled squares in Figure 3. The plot shows that the truncation bias is only less than 0,1 % at values of compression factor greater than about 0,97. Furthermore at $Z = 0,90$ the bias error may easily be as great as 2 %, reaching perhaps as much as 5 % at $Z = 0,85$.

These observations suggest that, even though a proper estimate of uncertainty carried out in accordance with the methods given ISO 6976 will take due account of these limitations of the modified IGT-32 method, there should nevertheless be a cut-off value of compression factor below which the method cannot be expected to provide reasonable (fit-for-purpose) results within the context of ISO 6976. The normative requirement set in ISO 6976 in order that calculations of the real-gas volumetric property calculations are valid is $1,00 \geq Z \geq 0,90$.

An alternative method for estimating the second contribution to $u(s_j)$ is available for some of the more important components, where reference quality equations of state (as reported in Reference [36] et seq.) are available within commercially available thermodynamic packages. For these components (for example methane, ethane, propane, nitrogen, carbon dioxide) it is straightforward to calculate both B_{jj} and Z_j directly and rigorously, without approximation, and then to compare the values of s_j calculated from these using Formulae (31) and (32). Results from this approach were found to compare well with those from the more widely applicable method.

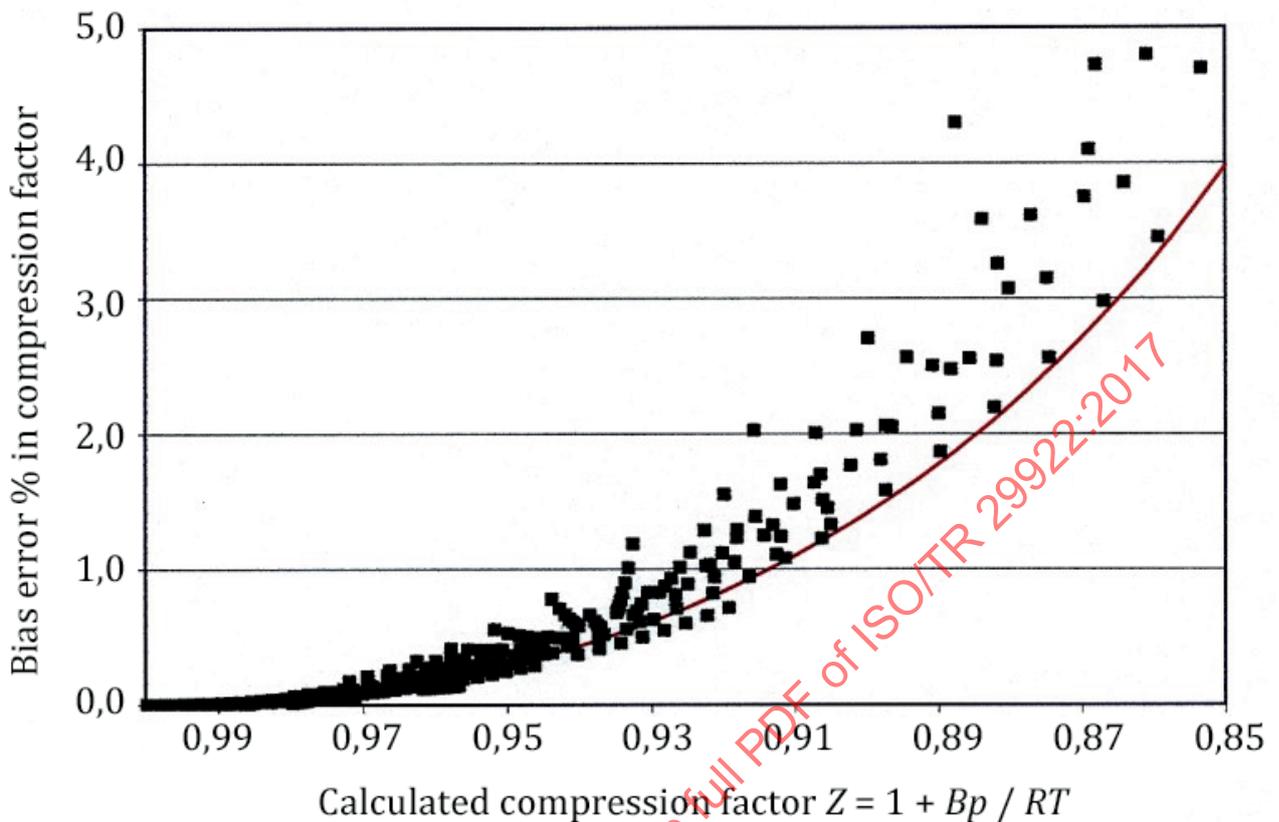


Figure 3 — Bias caused by truncation of the virial equation

8.4.3 Linearization error

[Figure 3](#) shows the extent to which the combined effects of truncation and linearization of the virial equation contribute, as bias, to the overall uncertainty in compression factor calculation.

It is, however, straightforward to calculate the linearization bias by itself, and thereby to separate out and assess the relative magnitudes of the two effects.

Suppose a value of compression factor Z is calculated using a notional value of B from the truncated and linearized virial equation (otherwise known as the truncated Berlin virial expansion) as follows

$$Z = 1 + B \cdot p / R \cdot T \quad (42)$$

This is the same (written slightly differently) as [Formula \(25\)](#).

The value of Z^+ that would be obtained from the same value of B (at the same state conditions of pressure p and temperature T) if this equation were left unlinearized (known as the truncated Leiden virial expansion) would then be

$$Z^+ = 1 + B \cdot p / Z^+ \cdot R \cdot T \quad (43)$$

This is the same (written slightly differently) as [Formula \(22\)](#). The bias error due to linearization is then simply $(Z - Z^+)$.

By eliminating $(B \cdot p / R \cdot T)$ between these two equations, Z^+ may be obtained as the positive solution to the quadratic equation

$$Z^2 - Z^+ + (1 - Z) = 0 \tag{44}$$

in which Z is taken as a disposable parameter. Table 5 shows the values of Z^+ and the bias error for $1,0 \geq Z \geq 0,85$. The locus of the values of percentage bias from this table is shown in Figure 3 as a continuous (red) line. The bias caused by truncation alone, i.e. by omission of the term containing the third virial coefficient, is then the difference between any of the plotted data points and the value given by the continuous line for the same value of Z .

Table 5 — Bias error caused by linearization of the virial equation

Z	Z^+	$Z - Z^+$	Bias %
1,00	1,000 0	0	0
0,99	0,989 9	0,000 1	0,010
0,98	0,979 6	0,000 4	0,041
0,97	0,969 0	0,001 0	0,103
0,96	0,958 3	0,001 7	0,177
0,95	0,947 2	0,002 8	0,295
0,94	0,935 9	0,004 1	0,436
0,93	0,924 3	0,005 7	0,613
0,92	0,912 3	0,007 7	0,837
0,91	0,900 0	0,010 0	1,099
0,90	0,887 3	0,012 7	1,411
0,89	0,874 2	0,015 8	1,775
0,88	0,860 6	0,019 4	2,205
0,87	0,846 4	0,023 6	2,713
0,86	0,831 7	0,028 3	3,291
0,85	0,816 2	0,033 8	3,976

Perhaps the main observation to be made in respect of these results is that, in general, the bias caused by linearization is more significant than the bias caused by truncation, although neither is negligible.

More specifically, the bias is less than 0,1 % for gases with $Z > 0,97$, and for gases with $Z > 0,99$, typical of virtually all treated natural gases of pipeline quality, the total bias is always less than 0,01 %.

8.4.4 Berlin versus Leiden

A simple alternative approach to some of the issues discussed in 8.4.2 and 8.4.3 may be given.

The Berlin and Leiden expansions for compression factor may be written respectively as

$$Z = 1 + B \cdot p / R \cdot T + \Phi_A(C, p, T) + \dots \quad (45)$$

(Berlin expansion),

$$\text{where } \Phi_A(C, p, T) = C \cdot (p/R \cdot T)^2 \quad (46)$$

and

$$Z = 1 + B / V + \Phi_B(C, V) + \dots \quad (47)$$

or

$$Z = 1 + B \cdot p / Z \cdot R \cdot T + \Phi_B(C, V) + \dots \quad (48)$$

(Leiden expansion),

$$\text{where } \Phi_B(C, V) = C / V^2 = C \cdot (p/Z \cdot R \cdot T)^2 \quad (49)$$

The combination of [Formula \(45\)](#) and [Formula \(48\)](#), and ignoring terms in the fourth and higher virial coefficients as being negligibly small, results in

$$(B / R \cdot T) \cdot (1/Z - 1) + [\Phi_B - \Phi_A] = 0 \quad (50)$$

For all gases under consideration herein (except for hydrogen, helium and neon), the compression factor $Z < 1$ and the second virial coefficient B is negative at all of the relevant reference conditions of pressure and temperature. Hence

$$\Phi_B(C, V) > \Phi_A(C, p, T) \quad (51)$$

Then, provided that both Φ_A and Φ_B are positive (which indeed is generally the case), it is thus apparent that the contribution of the third term in the virial expansion is greater for the Leiden formulation in molar volume V (or, equivalently, density) than for the Berlin formulation in pressure p .

To put it another way, this demonstrates in straightforward fashion that use of the truncated Berlin formulation provides a closer (less biased) approximation to un-truncated formulations than does using the truncated Leiden formulation – despite the fact that the latter is more correct in the sense of having a firmer basis in the framework of statistical mechanics. This feature is important in supporting the methodology adopted and described in [8.1.2](#) for the accurate derivation of pure component compression factors.

8.4.5 Hydrogen and helium

For hydrogen and helium (and neon) the question of how to assign values of summation factor s_j has already been discussed in [8.2.3](#). The assignment of the uncertainty $u(s_j)$ for these pseudo-values of s_j is also problematic. For each of these components ISO 6976:2016, Table 2 gives the value of $u(s_j) = 0,025$, calculated as

$$u(s_j) = -u(Z_j) / 2 \cdot s_j \quad (52)$$

with $u(Z_j)$ estimated conservatively (i.e. substantially over-estimated) as 0,000 5 and s_j taken as the previously adopted value of -0,01.

8.4.6 Water

One binary mixture for which the geometric-mean approximation for the interaction second virial coefficient [Formula (27)] is seriously invalid is methane-water, the result mainly of the strong polarity of the water molecule. This is potentially of some significance in the calculation of compression factor of a natural gas containing water vapour, most particularly for a water-saturated natural gas. In effect the invalidity of the geometric-mean assumption manifests itself as a bias, albeit small, in the compression factor.

NOTE The invalidity of the geometric-mean approximation is not restricted to the methane-water binary, but probably applies also to most binary interactions for which water vapour is one of the components.

A means has recently been suggested by Starling[55] by which the effect of this error may readily be offset, and thereby alleviated. In brief the concept is to replace the value of s_j (water), evaluated by the methods described in 8.1.2, by a value s_j^+ (which we may call a pseudo-value of s_j), calculated in such a way that the interaction second virial coefficient is correctly modelled at the expense of misrepresenting the second virial coefficient for the pure component water.

The logic of this is that, because of the relative amounts of water vapour (maximum mole fraction about 0,017 at 15 °C) and methane (mole fraction typically about 0,9), the frequency of water-methane molecular interactions is much greater than the frequency of water-water molecular interactions and, therefore, it is more important to model correctly the water-methane interaction than it is to model correctly the water-water interaction.

Such a pseudo-value s_j^+ may be readily evaluated as follows. If values of B_{1j} ($j = 1$ for methane) are known at the relevant metering temperatures, then the values of an 'interaction summation factor' s_{1j} may be calculated and the s_j^+ found in turn from

$$s_j^+ = (s_{1j})^2 / s_1 \text{ (methane)} \tag{53}$$

In fact, values of B_{1j} are not readily available in the range of metering reference temperatures but, by prudent extrapolation[55] of those indirect estimates that do exist[56], suitable values may be derived. This methodology leads to the following result for (as an example at 15 °C):

- s_1 (methane) = 0,044 52 (from ISO 6976:2016, Table 2);
- s_j (water) = 0,256 2 (from ISO 6976:2016, Table 2);
- s_j^+ (pseudo-water) = 0,063 5 (by calculation as above).

These values may in turn be used (again as an example at 15 °C) to calculate the compression factor by the methods of ISO 6976:2016 for a) pure methane, b) methane ($x_1 = 0,983 2$) near-saturated with water vapour ($x_j = 0,016 8$) and c) methane near-saturated with 'pseudo-water'. The results are as follows:

- a) Z (methane using s_1) = 0,998 02;
- b) Z (saturated using s_1 and s_j) = 0,997 69;
- c) Z (saturated using s_1 and s_j^+) = 0,997 99.

It is clear from this simple example that the modification to the treatment of water vapour leads to a value of compression factor for saturated methane that is much closer to that for dry methane than is the case for the unmodified treatment. A similar bias-offset would likewise apply to any realistic natural gas.

One issue that does arise in connection with the possible adoption of this scheme is how to set a value of uncertainty $u(s_j^+)$ to associate with the derived values of s_j^+ . It would seem proper that the value of $u(s_j^+)$ chosen should be of such magnitude as to include within its limits the "true" values of summation factor s_j for water vapour. This, however, would imply setting $u(s_j^+)$ to at least 0,25 (in order to cover $s_j = 0,3093$ at 0 °C) - some four times the value of s_j^+ itself and more than 15 times the estimate of uncertainty $u(s_j)$

given in ISO 6976:2016, Table 2. This seems rather strange, but is not entirely implausible and would not be impossible to adopt.

This scheme is attractive in both its simplicity and efficacy. Nevertheless it has not been adopted in ISO 6976:2016, largely because of the uncertainties inherent in the inference of interaction second virial coefficients from solubility data^[56], but also because of the uncertain effect of the modification to $s_j(\text{water})$ on the interaction virial coefficients of other components of a natural gas mixture. Not only that, but the *status quo* produces results that have, in general, always been considered as acceptably accurate.

8.4.7 Combination of uncertainties

The values of uncertainty $u(s_j)$ in s_j obtained by combining in quadrature the uncertainties from the two sources considered in 8.4.1 and 8.4.2 may readily be identified as the proper uncertainties to be associated with the pure components, but nevertheless they are still not those listed in ISO 6976:2016, Table 2. The values given there are larger than those estimated by the combination of these two sources. The reason for this is explained in 8.5.

8.5 Mixture uncertainty

As explained in 7.4, the third (and final) factor to be taken into account in the estimation of uncertainty in compression factor of a natural gas mixture is the additional uncertainty associated with the assumption [Formula (27)] that each interaction second virial coefficient B_{jk} is given by the geometric mean of the pure component second virial coefficients B_{jj} and B_{kk} . (In this respect, the special case of methane-water has already been discussed in 8.4.6.)

This uncertainty is in general accounted for in Formula (36) by the presence of the zero-value constant ζ with $u(\zeta) > 0$, but an entirely equivalent strategy is to associate an extra uncertainty with each value of s_j . Values for this extra uncertainty were estimated by comparing values of B_{1j} (that is, the interaction second virial coefficients with methane ($j = 1$) as one of the interacting pair) as calculated from Formula (27) with values listed for B_{1j} in Landolt-Börnstein^[28]. The difference between these values may be used as an estimate of the uncertainty in B_{1j} and converted directly into an uncertainty $u(s_j)$ in s_j .

Finally the uncertainty $u(s_j)$ in s_j estimated by this method may be combined in quadrature with the two independent contributions to uncertainty estimated by the methods described in 8.4 in order to arrive at an overall uncertainty $u(s_j)$ for each value of s_j . The resulting values are those that are listed in ISO 6976:2016, Table 2. The effect is that all the uncertainties in Z are subsumed within a single overall value of $u(s_j)$ for each component.

These values of $u(s_j)$ may then be used in the equations presented in ISO 6976:2016, Annex B (and in Clause 16) in order to provide estimates of the uncertainties in the relevant real-gas properties, namely calorific values, density, relative density and Wobbe indices, of the mixture.

9 Miscellaneous data

9.1 Atomic weights of the elements

9.1.1 Atomic weights 2007

The molar mass in $\text{kg}\cdot\text{kmol}^{-1}$ (in loose terminology, the relative atomic mass or atomic weight) of each of the atomic elements carbon, hydrogen, nitrogen, oxygen and sulfur is required for the calculation of the molar mass (loosely, the relative molecular mass or molecular weight) of each of the components considered in ISO 6976:2016.

The values of atomic weight given in Table 6 (which are repeated in ISO 6976:2016, A.2) are taken from the IUPAC (2007) recommendations^[57] and have been used in the derivation of the values of molar

mass listed in ISO 6976:2016, Table 1. The reasons for retaining these values of atomic weight when more recent pronouncements from IUPAC are available are discussed in 9.1.2.

The figure in the third column of Table 6 for each element is the uncertainty in atomic weight, here expressed (as reported in Reference [57]) not as the standard uncertainty but as the maximum credible deviation (resulting from the natural isotopic variation observed across a range of terrestrial samples) from the reported value of atomic weight. For the purpose of estimating the uncertainties in the molar masses as required for the calculation of uncertainties in the various physical properties according to ISO 6976:2016, each such value given for the uncertainty in atomic weight has been reinterpreted, following the example of Coplen et al.[58] and Picard et al.[59], as an expanded uncertainty with a coverage factor of at least two, and taken conservatively as two exactly.

For convenience, the atomic weights of the rare gases, needed in the calculation of the mean molecular weight of air, have been added to this table.

Table 6 — Atomic weights of the elements 2007

Element	Atomic weight $A/\text{kg}\cdot\text{kmol}^{-1}$	Expanded uncertainty $U(A)/\text{kg}\cdot\text{kmol}^{-1}$
carbon C	12,010 7	0,000 8
hydrogen H	1,007 94	0,000 07
nitrogen N	14,006 7	0,000 2
oxygen O	15,999 4	0,000 3
sulfur S	32,065	0,005
argon Ar	39,948	0,001
neon Ne	20,179 7	0,000 6
helium He	4,002 602	0,000 002
krypton Kr	83,798	0,002
xenon Xe	131,293	0,006

9.1.2 Atomic weights 2009 and 2011

Although the IUPAC (2007) set of recommendations for atomic weight values has been adopted for the particular requirements of ISO 6976:2016, it is not IUPAC's most recent pronouncement on the subject. Some explanation of why the IUPAC 2009[60] and 2011[61] recommendations have not been adopted in preference is necessary.

The 2009 IUPAC recommendations[60] recognize explicitly for the first time that, because of the natural (or engineered) terrestrial variations in isotopic abundance, the concept of atomic weight as a fundamental physical constant of an element having more than one stable isotope is false. For many elements accurate determinations of atomic weight on a selection of samples show a natural variation substantially greater than the precision of each determination. For this reason it is not possible to assign a definitive atomic weight to an element without knowledge of its isotopic composition. IUPAC has addressed this dilemma by citing a range, or interval, of atomic weights within which all natural terrestrial variations are expected to fall. The lower and upper bounds of these intervals are shown for carbon, hydrogen, nitrogen, oxygen and sulfur in columns 2 and 3 of Table 7.

IUPAC has further suggested a value, which they call the "conventional atomic weight", that may purportedly be taken as a purposeful mid-range value when the user has no knowledge of the isotopic distribution of his sample. This latter is the value given in column 4 of Table 7. It is, however, important to recognize that the so-called conventional atomic weight of an element cannot properly be identified as some specific kind of 'mean' or 'most likely' value.

Table 7 — Atomic weights of the elements 2009

Element	Atomic weight $A/\text{kg}\cdot\text{kmol}^{-1}$			Expanded uncertainty $U(A)/\text{kg}\cdot\text{kmol}^{-1}$	
	Lower bound	Upper bound	Conventional	Method B	Method C
carbon C	12,009 6	12,011 6	12,011	0,001	0,001 2
hydrogen H	1,007 84	1,008 11	1,008	0,001	0,000 16
nitrogen N	14,006 43	14,007 28	14,007	0,001	0,000 49
oxygen O	15,999 03	15,999 77	15,999	0,001	0,000 43
sulfur S	32,059	32,076	32,06	0,01	0,009 8
argon Ar			39,948	0,001	
neon Ne			20,179 7	0,000 6	
helium He			4,002 602	0,000 002	
krypton Kr			83,798	0,002	
xenon Xe			131,293	0,006	

As before, the standard atomic weights of the rare gases, which are unchanged from the 2007 values, have been added to column 4 of [Table 7](#).

The figures given in the fifth and sixth columns are estimates of the expanded uncertainty for each element. For each of the rare gases this has been derived, as before, from the maximum credible deviation from the standard atomic weight resulting from natural isotopic variation, and is unchanged.

For the more important top five components, however, it is not this simple. The following is a direct quotation from the 2009 IUPAC documentation^[60] – “These conventional values have no uncertainty values associated with them. They have been selected so that most or all natural terrestrial atomic weight variation is covered by an interval of plus or minus one in the last digit”.

This specification – actually more a disclaimer – seems to leave open at least three possibilities for users who need to incorporate an estimate of uncertainty into their calculation, as follows –

A. Set the standard uncertainty $u(A) = 0$. At first sight this seems an incongruous and impossible choice (and it is), but in another sense it fits logically with the concept of A as nothing more than a conventional fixed (fiducial) value. Nevertheless, it is physically nonsensical, and this option is discounted.

B. Set the expanded uncertainty $U(A) = \pm 1$ in the last quoted digit, as given in [Table 7](#) column 5. This choice seems to correspond more closely with what is intended by the authors of Reference [60], but the question is left open of what value of the coverage factor k is to be inferred.

C. Make some sort of estimate of $U(A)$ for each element based on the observed range of values of A (columns 2 and 3 of [Table 7](#)). This seems to be the most technically sound option, but any such estimate needs properly to involve the interpretation of the interval between the upper and lower bounds in terms of some form of distribution. The basis on which such an interpretation should be made is not entirely clear.

For the purposes of [Table 7](#) column 6, option C has been evaluated, with the upper and lower bounds of the atomic weight distribution for each element assumed to be the limits of a rectangular distribution. The standard uncertainty is then given by half the interval divided by the square root of three^[62], and the expanded uncertainty as twice this value. The resulting values of expanded uncertainty are given in column 6 of [Table 7](#) to two significant figures.

For carbon and sulfur the two methods B and C give similar results, but for nitrogen and oxygen method B gives estimates about twice those of method C, while for hydrogen the difference is over sixfold.

Furthermore, it is clear that, whichever method is used, the IUPAC (2009) uncertainties are all significantly greater than the IUPAC (2007) uncertainties. The increase in uncertainty is least for

carbon (about 25 % by method C), while for the other elements the increase is generally by a factor of around two for method C and greater still by method B.

The only reasonable way in which it might be possible to achieve comparable uncertainties between the two years would be to interpret either “plus or minus one in the last digit” or the observed difference between the upper and lower bounds as three standard deviations of a normal Gaussian distribution, but there is no obvious rationale for this.

9.1.3 Discussion

It is not difficult to understand why IUPAC has taken the direction it has in respect of atomic weights. Their new approach is undoubtedly and absolutely correct in a technical sense. Nevertheless the way in which it has been implemented and presented leaves what might be termed the ‘gas analysis and natural gas metrology community’ with a major problem. The problem is not of understanding but of interpretation and detail.

Close inspection of the distribution diagrams given for each of the relevant elements in the IUPAC (2009 and 2011) recommendations^{[60][61]} shows without doubt that the conventional values, and in particular the associated uncertainties, place too much emphasis, for the purposes of ISO 6976:2016, on inorganic and geological samples, which generally exhibit much wider ranges of atomic weight (isotopic) variation than found with other sources. Samples that refer specifically to natural hydrocarbon and similar deposits are much more limited in the observed ranges of atomic weights of the constituent elements.

This observation does not support the truncation of atomic weights to just three decimal places (two for sulfur) and, even more so, does not support the use of “plus or minus one in the last digit” (or indeed of the upper and lower bounds of observed values) as a reasonable measure of uncertainty. This conclusion applies in general to many gas metrology applications, but in particular to the present revision of ISO 6976.

Furthermore, there seem to have been no changes to the underlying isotope distribution data on which the recommendations are based for any of the CHNOS elements between 2007 and 2009 or 2011. That being so, it is even harder to see any compelling logic to abandon the 2007 recommendations; in other words, if nothing has changed, then what was good enough then should be good enough now.

There are also a number of specific “objections” to the use of conventional atomic weights in the present application, as follows

- a) for hydrogen, the expanded uncertainty calculated as described above from the range of observations (method C) is (possibly) sensible enough, but IUPAC’s recommendation of “plus or minus one in the last digit” (method B) implies a potential range of atomic weight values (0,002) of seven-and-a-half times the maximum range observed to date (0,000 27), and
- b) if the method B uncertainty for hydrogen were to be adopted, then for typical hydrocarbons of the kind found in natural gases, containing many atoms of hydrogen, the uncertainty in molecular weight would be falsely dominated by this quantity,
- c) for oxygen, the conventional atomic weight selected by IUPAC falls incongruously outside of the range of observations,
- d) for sulfur, although the conventional atomic weight selected by IUPAC is within the range of observations, it is very close to the lower extreme of that range.

To summarize all of this, neither the values nor the associated uncertainties given by the most recent (2009 and 2011) IUPAC atomic weight recommendations^{[60][61]}, properly match the requirements of the gas metrology community. For this reason the values of atomic weights and the associated uncertainties adopted for ISO 6976:2016 are the standard (2007) values given in [Table 6](#).

Another argument in favour of retaining the IUPAC (2007) recommendations relates to the need (or at least desirability) to retain consistency throughout the suite of standards produced by ISO/TC 193 for the calculation of a range of physical properties of natural gas. All of the pre-existing and currently

valid standards in this collection use atomic weights numerically equal to the IUPAC (2007) recommendations.

Nevertheless, rejection of the learned and authoritative IUPAC recommendations is hardly a satisfactory situation. One might hope therefore that the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) will address some of the issues raised by the gas metrology community in its future deliberations. Perhaps the inclusion of one more digit in the conventional atomic weights and a more considered analysis of uncertainties will go some way towards solving these issues, or perhaps a subset of atomic weights, including uncertainties, aimed more specifically at the gas metrology community might be devised (and it could be done).

Meanwhile the debate within the community of gas analysis and natural gas metrologists is ongoing. A useful contribution to this debate has been made recently by van der Veen and Hafner^[63]. This document discusses some of those points alluded to above along with several others that will not be elaborated here.

One particularly important comment, however, made as early as the abstract to these authors' main text, is that "... the atomic weight intervals (given in the 2009 and 2011 recommendations) include sources that are unlikely to be generally relevant for measurements supporting trade, commerce, health and safety ..." ^[63]. Self-evidently this stricture applies directly to natural gas metrology. Another issue spelled out very clearly is that, whatever the (unknown) distribution of isotopic abundances for any particular element within its upper and lower bounds of atomic weight, that distribution will certainly not be rectangular and, therefore, any uncertainty estimate based upon this assumption is bound to be false.

The debate continues but, so far as ISO 6976:2016 is concerned, use of the 2007 atomic weights remains the chosen option. It is, essentially, an issue of fitness-for-purpose.

9.2 Composition and molecular weight of dry air

The recommended molar composition of dry air is given in [Table 8](#). This is taken from the work of Picard et al.^[59], and is *not* the same as given in ISO 6976:1995. Note also that the molar composition differs from the volumetric composition.

Table 8 — Molar composition of dry air

Component	Mole fraction
nitrogen	0,780 848
oxygen	0,209 390
argon	0,009 332
carbon dioxide	0,000 4
neon	0,000 018 2
helium	0,000 005 2
methane	0,000 001 5
krypton	0,000 001 1
hydrogen	0,000 000 5
nitrous oxide	0,000 000 3
carbon monoxide	0,000 000 2
xenon	0,000 000 1

When this composition is used in conjunction with the values of molar mass for the individual components as given in ISO 6976:2016, Table 1, the resulting value for the molar mass of dry air rounded to the fifth decimal place is

$$M_{\text{air}} = (28,965\ 46 \pm 0,000\ 17) \text{ kg}\cdot\text{kmol}^{-1}$$

Here the uncertainty has been calculated (as a standard uncertainty) as the mole fraction weighted sum of the standard uncertainties in the component molecular weights combined in quadrature, as follows:

$$u(M_{\text{air}}) = \sqrt{\sum_{j=1}^{10} [x_j \times u(M_j)]^2} \quad (54)$$

where x_j is the mole fraction of the j -th component of dry air and the summation is over all 10 components listed in [Table 8](#). The values for $u(M_j)$ have mostly been calculated by the method described in ISO 6976:2016.

Another factor, not accounted for in the above, that has the potential to influence the uncertainty of M_{air} is the uncertainty in the composition. The component mole fractions of air may vary slightly from place to place, more particularly in a laboratory environment as opposed to the open air. However, given that the mole fractions listed are intended to constitute a 'standard' composition, it seems inappropriate to make any further allowance in the present context.

NOTE It seems incongruous that the standard uncertainty of the molar mass of air (0,000 17 kg·kmol⁻¹) is less than that of pure molecular nitrogen (0,000 20 kg·kmol⁻¹), but it is right. The underlying reason is that the composition of air is, for the purposes of ISO 6976:2016, taken to be without uncertainty. This calculation implicitly assumes no correlation between the molar mass values for any of the components. Although this assumption is not valid for molecular oxygen and carbon dioxide (both contain oxygen atoms), carbon dioxide is present in such a small concentration that there is no tangible effect on the result.

In reality, the only significant variation in the composition of air is for the mole fraction of carbon dioxide. The value given in [Table 8](#) may be considered as an open-air minimum. Due mainly to human activities, it may vary locally from place to place and is known globally to be increasing slowly over time. It is usual to assume that any carbon dioxide present in excess of that figure displaces an equal amount of oxygen from the atmosphere. Thus if the prevailing mole fraction x_{CO_2} of carbon dioxide is known, then the molar mass of dry air may be recalculated as

$$M_{\text{air}} = 28,965\ 46 + 12,011 (x_{\text{CO}_2} - 0,000\ 4) \text{ kg}\cdot\text{kmol}^{-1} \quad (55)$$

It is reiterated, however, that ISO 6976:2016 deals only with dry air of reference composition and that recalculation according to [Formula \(55\)](#) is beyond its scope.

10 Effects of water vapour on calorific value

10.1 Preamble

The presence of water vapour in a natural gas mixture, whether present at source (i.e. at the point of sampling) or introduced (or removed) as part of a measurement procedure, is a complicating factor in the determination of its calorific value. This clause aims to clarify the issues involved in understanding the proper status of a measured calorific value in circumstances where the gas is not "dry" from start to finish.

Most traditional old-style combustion calorimeters used for the direct measurement of calorific value per unit volume saturate the fuel gas with water vapour before combustion (i.e. during metering), and will therefore measure, and probably (but not necessarily) report, calorific values on an (assumed) saturated basis. Such values are lower than those for the unsaturated (dry or partially saturated) gas because, in simple terms, of the displacement of fuel gas by water vapour in the metering system.

Other (somewhat more modern) instruments used for either the direct or indirect determination of calorific value may not function in the same way. For example:

- some direct combustion calorimeters burn the gas on an "as received" basis (i.e. with its prevailing water vapour content) and report the actual calorific value, but on an (assumed) dry basis;

- some instruments dry the gas prior to calorific value determination, and so measure and report a dry gas value even though the gas may originally have contained water vapour;
- instruments for component-analysis of gases (in particular gas-chromatographs) usually analyse for all important components with the single exception of water, and so a calculated calorific value is reported on the dry basis even though the gas may actually contain water vapour.

For a more detailed discussion of the various operational techniques employed currently (and historically) in the instrumental determination of volume-basis calorific value, see ISO 15971:2008^[64].

In order to make valid comparisons of gas calorific values determined by different techniques, it is necessary therefore to take into account:

- the degree of saturation with water vapour of the gas in its original state;
- the degree of saturation with water vapour of the gas during the measurement procedure (i.e. after metering);
- the operational characteristics of the measurement instrument or procedure; and
- the degree of saturation with water vapour of the gas referred to in the reported calorific value.

When all of these factors are known, it is possible to refer all determinations of calorific value to a uniform and consistent basis.

The most logical basis for either measurement or calculation would seem, in general, to be the “as received” basis, in which the calorific value is determined, and quoted, with any water vapour present considered simply as a distinct component of the mixture, neither more nor less “special” than any other component, and present at a definite known mole fraction.

There are three considerations to take into account in making calculations if this approach is adopted, especially if analysis for water vapour does not form part of the primary analytical procedure (i.e. if its amount has to be inferred by secondary means such as hygrometric or dewpoint measurement). These are now considered in 10.2 to 10.4 in order of decreasing significance.

10.2 Excluded volume effect.

Water may be present in natural gas at a partial pressure p_w of up to its saturation vapour pressure $p_s(t_2)$ at the reference temperature t_2 of the gas metering system. The conventional - and correct - way of viewing such water vapour is to consider it as excluding a proportion p_w/p_2 of the metering volume from the dry fuel gas proper, thereby reducing the determined calorific value by this proportion to the value

$$Hv(\text{measured}) = Hv(\text{dry gas}) \cdot (p_2 - p_w) / p_2 \quad (56)$$

where Hv is the calorific value (either gross or net) on the volume basis.

In respect of the calculation of calorific value from composition, an entirely equivalent way of viewing this effect, but preferable because it now becomes more clear that the calorific value Hv in [Formula \(56\)](#) may with equal validity be replaced by Hc , the calorific value on a molar basis, or by Hm , the calorific value on a mass basis, is to proceed in terms of mole fractions.

Suppose a mole fraction analysis of the gas, excluding any water vapour, is known. If the partial pressure of water vapour in the sample is now somehow determined, its mole fraction may be taken as p_w/p_2 . In order to retain the mole fraction sum for the whole mixture as unity, the mole fraction of each other component is necessarily revised (normalized) by multiplication by the factor $(1 - p_w/p_2)$.

Thus, since the calculated calorific value is a summation of terms linear in component mole fractions, the calculated calorific value is simply reduced by this proportion (except for the secondary effects referred to in [10.3](#) and [10.4](#)), just as is seen from the previous, more traditional, viewpoint.

Of course, if the original mole fraction analysis includes water vapour, then its alternative determination by this approach is not relevant.

This primary effect is important, as the following example shows. Suppose we wish to calculate the calorific value on a saturated-gas basis from a dry-gas analysis, in order perhaps to make a meaningful comparison between the dry-gas calorific value and that determined by a calorimeter that saturates the same gas during metering. Suppose also that the dry-gas volume-basis calorific value is $38,00 \text{ MJ}\cdot\text{m}^{-3}$ at combustion and metering reference conditions of $15 \text{ }^\circ\text{C}$, $101,325 \text{ kPa}$. At this condition the saturation vapour pressure is $1,706 \text{ kPa}$ (see [Table 9](#)), and the mole fraction of water in natural gas saturated with water at the reference conditions is therefore

$$x_w = 1,706/101,325 = 0,016 837$$

Thus the saturated-gas calorific value (ignoring the secondary effects discussed in [10.3](#) and [10.4](#)) is less than the dry-gas calorific value by the factor $(1 - 0,016 837)$. That is

$$(Hv)_G(\text{saturated}) = 38,00 \times 0,983 163 = 37,36 \text{ MJ}\cdot\text{m}^{-3}$$

With differences between dry and saturated calorific values (for $t_2 = 15 \text{ }^\circ\text{C}$) of some 1,68 %, and with partially-saturated calorific values (for gases with water vapour present at below its saturation pressure) residing somewhere between the two extremes, it is obviously very important to consider the way in which water vapour is accounted for by the measurement or analysis technique.

A situation calling for especial care can arise for a gas containing water vapour as a known component at below its saturation vapour pressure. In this case the dry-gas, as received (partially saturated) and saturated-gas calorific values are all calculable, all different and all capable of being confused one with another.

NOTE For other metering temperatures (all at a metering pressure of $p_2 = 101,325 \text{ kPa}$), the mole fractions of water vapour present at saturation are $0,006 0$ ($t_2 = 0 \text{ }^\circ\text{C}$), $0,017 4$ ($t_2 = 60 \text{ }^\circ\text{F}$) and $0,023 1$ ($t_2 = 20 \text{ }^\circ\text{C}$), i.e. the maximum limit of reduction in calorific value caused to an otherwise dry gas by the presence of water vapour is $0,60 \text{ } \%$, $1,74 \text{ } \%$ and $2,31 \text{ } \%$ respectively.

10.3 Latent heat (enthalpic) effect

A secondary effect of the presence of water vapour in a sample gas is ignored in [10.2](#). The latent heat of vaporization of the water produced by the combustion of hydrocarbons is a significant factor in the determination of the calorific value of those hydrocarbons and, consequently, the state of that water is precisely defined in ISO 6976:2016, 3.1 and 3.2.

In the case of the gross calorific value it is required that all the water produced by the combustion reaction is condensed to the liquid state at the combustion reference temperature t_1 . This requirement may be impractical, but it does provide a sensible theoretical basis for the calculation of gross calorific value for a dry natural gas. However, the presence of water vapour in the gas volume prior to combustion presents a problem of how to treat the state of that water after combustion:

- a) is it to be assumed that this water remains gaseous after combustion, thus having no effect on the total energy (heat of combustion) released i.e. only the water 'formed by combustion' is condensed,
- b) is it to be assumed that this water is also condensed to the liquid state at the combustion reference temperature t_1 , thereby enhancing the heat of combustion by an amount equal to the released latent heat of vaporization of water, or
- c) is it to be assumed that the products of combustion carry away just sufficient water vapour to satisfy exactly the saturation vapour pressure p_s at the combustion reference temperature t_1 .

All three of these alternatives are, to a greater or lesser extent, unrealistic and/or impractical. There is however a strong argument in favour of the simplest treatment which, for the gross calorific value, is to assume that all water, both that contained in the gas volume prior to combustion and that produced by combustion, is condensed to the liquid state at the combustion reference temperature t_1 , i.e. option b).

Logic as well as simplicity seems also to be in favour of option b). Option c) would be virtually impossible to implement in routine calculations and is not considered further.

It may be remarked in passing that option a) corresponds to the strict interpretation of the definition of gross calorific value given in the second edition of ISO 6976 whereas option b) corresponds to the revised definition given in ISO 6976:2016.

In the case of option b) it is clear that the water vapour contained in the sample gas volume must again be treated simply as one component of the natural gas, present at a specific and known mole fraction, and having a pseudo-calorific value derived from the latent heat of vaporization of water. In other words there is an additional $x_j \cdot H_j$ term, for water, in the usual mole-fraction weighted summation. That is why the gross calorific value given for water vapour in ISO 6976:2016, Table 3 is not zero.

Such a treatment results in a small but non-negligible enhancement of calorific value. Assuming saturation with water vapour, the enhancement is independent of gas composition, almost independent of the combustion reference temperature t_1 , and dependent almost entirely on the gas volume (metering) temperature t_2 . For the volume-basis calorific value, the enhancement for a saturated gas is

- for metering (and combustion) at 0 °C an enhancement of 0,012 MJ·m⁻³,
- for metering (and combustion) at 15 °C an enhancement of 0,032 MJ·m⁻³,
- for metering (and combustion) at 60 °F an enhancement of 0,033 MJ·m⁻³, and
- for metering (and combustion) at 20 °C an enhancement of 0,042 MJ·m⁻³.

For net calorific value, all water vapour remains in the gas phase, and so there is no enthalpic effect of this sort to consider.

10.4 Compression factor effect

There is a third (even more minor) effect, but one which should nevertheless be taken into account. The presence of water vapour affects the compression factor Z of the mixture, and thus alters the real-gas volume-basis calorific value by a calculable amount.

At 15 °C, for example, Z (as calculated in accordance with ISO 6976:2016) is changed from dry to saturated by only about 4 parts in 10000 (from 0,998 1 to 0,997 7) for a typical natural gas – but that still implies a (possibly) non-negligible enhancement of 0,015 MJ·m⁻³ for a gas of 38,00 MJ·m⁻³. In this context, however, see also [8.4.6](#).

10.5 Combination of effects

In short, in the event that it is necessary to make calculations for natural gas containing water vapour, then the points discussed in [10.2](#) to [10.4](#) should all be taken into account when deciding upon the approach that is best suited to the purpose and intent of the calculations.

Much of the somewhat discursive content of these subclauses may be summarized in a single equation that relates the gross calorific value of a dry gas to the gross calorific value of the same gas when saturated with water vapour, as follows:

$$\begin{aligned} (Hv)_G(\text{sat}) &= (Hv^o)_G(\text{sat}) / Z(p_2, t_2, \text{sat}) \\ &= \left[(Hv^o)_G(\text{dry}) \cdot \left(1 - \frac{p_s(t_2)}{p_2} \right) + L^o(t_1) \cdot \left(\frac{p_s(t_2)}{p_2} \right) \cdot \left(\frac{p_2}{R \cdot T_2} \right) \right] \times \frac{1}{Z(p_2, t_2, \text{sat})} \end{aligned} \quad (57)$$

This equation may be further generalized to the case where the sample gas contains water vapour at a known partial pressure p_w less than the saturation vapour pressure p_s or at a known mole fraction x_w , as follows:

$$(Hv)_G(\text{wet}) = \left[(Hv^o)_G(\text{dry}) \cdot \left(1 - \frac{p_w(t_2)}{p_2} \right) + L^o(t_1) \cdot \left(\frac{p_w(t_2)}{p_2} \right) \cdot \left(\frac{p_2}{R \cdot T_2} \right) \right] \times \frac{1}{Z(p_2, t_2, x_w \neq 0)} \quad (58)$$

where

x_w is equal to p_w/p_2 ;

p_w is the partial pressure of water vapour at the metering reference temperature t_2 ;

p_s is the saturation vapour pressure of water at the metering reference temperature t_2 ;

p_2 is the metering reference pressure, most commonly 101,325 kPa (1 standard atmosphere = 14,695 95 ... psia);

L^o is the standard enthalpy of vaporization of water at the combustion reference temperature t_1 , where the factor $(p_2/R \cdot T_2)$ has been applied to convert this from the molar to the ideal volumetric basis;

$p_s > p_w > 0$.

Other values of the metering reference pressure that are in more occasional use include the following (see also 14.3):

- 101,374 kPa (30 inches Hg at 60 °F and gravity for latitude 53 degrees north)
- 101,560 kPa (14,73 psia – US customary pressure)
- 101,592 kPa (30 inches Hg at 32 °F and standard gravity)

Values of p_s (calculated using Reference [34]) and L^o (taken from ISO 6976) at the reference temperatures of interest are given in Table 9.

Table 9 — Saturation vapour pressure and standard enthalpy of vaporization of water at various reference temperatures

	Reference temperature				
	0 °C	15 °C	60 °F	20 °C	25 °C
p_s/kPa	0,611	1,706	1,768	2,339	
$L^o/\text{kJ}\cdot\text{mol}^{-1}$	45,064	44,431	44,408	44,222	44,013

10.6 Spectator water

Spectator water is terminology used, most commonly in north America [65][66], to describe water vapour present in either a gas mixture or in air used for combustion (or both), and which passes through the combustion process unchanged.

In the strictest interpretation of the word ‘unchanged’ it is taken to mean unchanged in both chemical and physical condition, i.e. water vapour remains as water vapour throughout and, for gross calorific value, only the water formed by combustion is condensed. Self-evidently, this interpretation corresponds to the definition of gross calorific value as envisaged in option a) of 10.3.

NOTE 1 In GPA 2172-09 [66], spectator water is defined as ‘... water carried by the gas or air that feeds the combustion reaction. Spectator water does not contribute to the gross heating value.’

NOTE 2 In ISO 6976:2016, whereas any water in a gas sample is assigned a notional enthalpy of combustion numerically equal to its enthalpy of vaporization, spectator water can instead be treated formally as a pseudo-component having zero enthalpy of combustion.

A more relaxed interpretation of 'unchanged' is to allow any water present in the gas sample to condense to the liquid state, i.e. it is only unchanged in the chemical sense. This interpretation corresponds to the definition of gross calorific value as envisaged in option b) of [10.3](#).

Of course, this latter interpretation ignores the question of how to account for any water vapour present in the combustion air. However, this is not an issue that properly needs to be considered here. In the definition of gross calorific value given either by option a) (as in 2nd edition ISO 6976) or option b) (3rd edition) there is an implicit assumption that the air or (more correctly) oxygen used for combustion is dry and of the correct stoichiometric amount to satisfy the combustion equation.

If this were not the case calorific value, far from being a well-defined and descriptive property of a gas mixture, would be a variable dependent upon the condition (and excess amount) of the air used for combustion.

Nevertheless, it is true that the amount of heat released by a practical (real-life) combustion reaction in which the air is not dry depends upon both the water content (humidity) and excess amount of the air and upon whether the initial water vapour content of the air is condensed, partially condensed or remains in the vapour state after combustion.

The issues involved, which go beyond the scope of ISO 6976, are discussed in [10.7](#).

10.7 Effect of humid air

10.7.1 Preamble

If the air used for combustion is not dry then the amount of heat released in the combustion process will depend sensibly upon the quantity of air used (including any excess to that required for stoichiometric combustion), its degree of saturation (humidity), and the final state to which the water vapour content is taken. It is useful to set up a formalism that models such a situation. The analysis given here is simplified by the implicit assumption that the combustion process involves only ideal fluids i.e. that small effects resulting from enthalpy of mixing and volume of mixing are excluded.

It is perhaps instructive to build up the analysis in stages of increasing complexity, as presented in the following subclauses.

10.7.2 Stoichiometric combustion with oxygen

For simplicity, consider the combustion of an N -component hydrocarbon gas mixture modelled as a (single-component) pseudo-hydrocarbon gas C_aH_b , where a and b are in general non-integer values of the atomic indices given by

$$a = \sum_{j=1}^N x_j \cdot a_j \quad (59)$$

and

$$b = \sum_{j=1}^N x_j \cdot b_j \quad (60)$$

Then the stoichiometric combustion equation for one mole of C_aH_b , with the water of combustion to be condensed, is



where $\theta = a + b/4$.

The heat released per mole of C_aH_b is equal to the gross calorific value (as defined in ISO 6976:2016) on a molar basis $(Hc)_G(\text{dry})$.

10.7.3 Combustion of dry gas with excess dry air

In this case the combustion equation may be written as



where $(\text{air}) = \alpha N_2 + \beta O_2 + \gamma Ar$

with (roughly and for simplicity, see [Table 8](#) for more exact values)

$$\alpha = 0,78, \beta = 0,21, \gamma = 0,01$$

and ε is molar amount of air (including any excess) per mole of reactant.

NOTE Provided that $\varepsilon > (\theta/\beta)$ there is always sufficient oxygen for complete combustion.

Because each of the three components (nitrogen, argon and excess oxygen) represented in the third term on the right-hand side of [Formula \(62\)](#) leave the reaction in the same physical state as they entered, i.e. as gases at (p_2, t_2) , there is no net release of heat associated with their presence, and the total heat released by the reaction is again simply $(Hc)_G(\text{dry})$.

10.7.4 Combustion of wet gas with excess dry air

In this case the combustion equation may be written as

$$\begin{aligned} & (1 - x_w) C_a H_b + x_w H_2O(\text{vap}) + \varepsilon(\text{air}) \\ & = a \cdot (1 - x_w) CO_2 + [(b/2) \cdot (1 - x_w) + x_w] H_2O(\text{liq}) + [\varepsilon(\text{air}) - \theta \cdot (1 - x_w) O_2] \end{aligned} \quad (63)$$

where x_w is the mole fraction of water vapour present in the gas sample, given by

$$x_w = p_w/p_2 = \xi_g \cdot p_s/p_2 \quad (64)$$

in which p_w , p_s and p_2 are as given below [Formula \(58\)](#) and ξ_g is the relative humidity of the gas sample.

The heat released in this reaction is given by

$$\begin{aligned} (Hc)_G(\text{wet}) &= (1 - x_w) \cdot (Hc)_G(\text{dry}) + x_w \cdot L^o \\ &= (1 - \xi_g \cdot p_s/p_2) \cdot (Hc)_G(\text{dry}) + (\xi_g \cdot p_s/p_2) \cdot L^o \end{aligned} \quad (65)$$

Note how directly this equation compares with [Formula \(58\)](#) for the volume-basis gross calorific value.

10.7.5 Combustion of wet gas with excess humid air

In order to take into account the effect of humid air used for combustion it is necessary to rewrite the composition of air as follows:

$$(\text{air})^+ = \alpha^+ N_2 + \beta^+ O_2 + \gamma^+ Ar + \delta H_2O(\text{vap})$$

where $\delta = \xi_{\text{air}} \cdot p_s/p_2$, in which ξ_{air} is the relative humidity of the air and

$$\alpha^+ = \alpha (1 - \xi_{\text{air}} \cdot p_s/p_2)$$

$$\beta^+ = \beta (1 - \xi_{\text{air}} \cdot p_s/p_2)$$

$$\gamma^+ = \gamma (1 - \xi_{\text{air}} \cdot p_s/p_2)$$

The combustion formula is

$$\begin{aligned} & (1 - x_w) C_a H_b + x_w H_2O(\text{vap}) + \varepsilon(\text{air}) + \\ & = a \cdot (1 - x_w) CO_2 + [(b/2) \cdot (1 - x_w) + x_w + \varepsilon \cdot \delta] H_2O(\text{liq}) + [\varepsilon(\alpha^+ + \beta^+ + \gamma^+) - \theta \cdot (1 - x_w) O_2] \end{aligned} \quad (66)$$

which may be rewritten as

$$\begin{aligned} & (1 - \xi_g \cdot p_s/p_2) C_a H_b + (\xi_g \cdot p_s/p_2) H_2O(\text{vap}) + \varepsilon(\text{air}) \cdot (1 - \xi_{\text{air}} \cdot p_s/p_2) + [\varepsilon \cdot \xi_{\text{air}} \cdot p_s/p_2] H_2O(\text{vap}) \\ & = a \cdot (1 - \xi_g \cdot p_s/p_2) CO_2 + [(b/2) \cdot (1 - \xi_g \cdot p_s/p_2) + \xi_g \cdot p_s/p_2 + \varepsilon \cdot \delta] H_2O(\text{liq}) \\ & + [\varepsilon(\text{air}) \cdot (1 - \xi_{\text{air}} \cdot p_s/p_2) - \theta \cdot (1 - \xi_g \cdot p_s/p_2) O_2] \end{aligned} \quad (67)$$

The heat released per mole by this reaction is given by

$$(Q)_G = (1 - \xi_g \cdot p_s/p_2) \cdot (Hc)_G(\text{dry}) + [(\xi_g \cdot p_s/p_2) + \varepsilon \cdot \delta] \cdot L^o$$

$$= (1 - \xi_g \cdot p_s/p_2) \cdot (Hc)_G(\text{dry}) + [(\xi_g \cdot p_s/p_2) + (\varepsilon \cdot \xi_{\text{air}} \cdot p_s/p_2)] \cdot L^o \quad (68)$$

It is self-evidently not possible to calculate $(Q)_G$ unless the values of ξ_g , ξ_{air} and ε are known. The latter quantity in particular is unlikely to be well known. This is perhaps unfortunate, because even the question of whether $(Q)_G$ is less than or greater than $(Hc)_G(\text{dry})$ depends largely upon the magnitude of ε .

Even if these values are known, however, it is still not a complete solution to the issue of what happens in practice. This is because, rather than all of the water present after combustion condensing to the liquid state, some is inevitably carried away as vapour in the exhaust gases.

The assumption that the exhaust gases are fully saturated with water vapour at the combustion reference conditions allows this circumstance to be accounted for by a simple modification to [Formula \(67\)](#) as follows.

The first (carbon dioxide) and third (excess air) terms on the right-hand side of [Formula \(67\)](#) are, as written there, unsaturated. The total molar amount of these gases is

$$\varphi = a \cdot (1 - \xi_g \cdot p_s/p_2) + [\varepsilon \cdot (1 - \xi_{\text{air}} \cdot p_s/p_2) - \theta \cdot (1 - \xi_g \cdot p_s/p_2)] \quad (69)$$

The molar amount of water vapour that these gases are able to carry away at saturation is then given by $(p_s/p_2) \cdot \varphi$ and, in place of [Formula \(67\)](#), may now be written

$$(1 - \xi_g \cdot p_s/p_2) C_a H_b + (\xi_g \cdot p_s/p_2) H_2O(\text{vap}) + \varepsilon(\text{air}) \cdot (1 - \xi_{\text{air}} \cdot p_s/p_2) + [\varepsilon \cdot \xi_{\text{air}} \cdot p_s/p_2] H_2O(\text{vap})$$

$$= a \cdot (1 - \xi_g \cdot p_s/p_2) CO_2 + (p_s/p_2) \cdot \varphi H_2O(\text{vap})$$

$$+ [(b/2) \cdot (1 - \xi_g \cdot p_s/p_2) + \xi_g \cdot p_s/p_2 + \varepsilon \cdot \delta - (p_s/p_2) \cdot \varphi] H_2O(\text{liq})$$

$$+ [\varepsilon(\text{air}) \cdot (1 - \xi_{\text{air}} \cdot p_s/p_2) - \theta \cdot (1 - \xi_g \cdot p_s/p_2) O_2] \quad (70)$$

The heat released by this reaction is given by

$$(Q)_G = (1 - \xi_g \cdot p_s/p_2) \cdot (Hc)_G(\text{dry}) + [(\xi_g \cdot p_s/p_2) + \varepsilon \cdot \delta - (p_s/p_2) \cdot \varphi] \cdot L^o$$

$$= (1 - \xi_g \cdot p_s/p_2) \cdot (Hc)_G(\text{dry}) + [(\xi_g \cdot p_s/p_2) + (\varepsilon \cdot \xi_{\text{air}} \cdot p_s/p_2) - (p_s/p_2) \cdot \varphi] \cdot L^o \quad (71)$$

This quantity is never likely to be easy to evaluate on a routine basis but, in principle and subject mainly to knowledge of ε , is not impossible.

The extension of this kind of analysis from a generalized pseudo-hydrocarbon $C_a H_b$ to a generalized pseudo-compound $C_a H_b N_c O_d S_e$ is straightforward but tedious and unrewarding.

It is important to reiterate that none of the analysis given in this subclause in any way modifies or extends the interpretation of calorific value, which is fully and properly defined in ISO 6976:2016.

11 Summary, discussion and selection of the calorific value of methane

11.1 Standard enthalpy of combustion

11.1.1 Background

The heat (enthalpy) of combustion of methane is unarguably the single most important physical property value used in the determination of the calorific value of natural gas. Not only is methane the major component of natural gas but ultra-high purity methane is frequently used as a calibration gas for many types of calorimeter used routinely to measure the calorific value of natural gas.

The heat of combustion of methane was first determined in 1848, and 11 studies, spread thinly over 160-odd years, have now been reported. However, six of the early studies (1848-1932) can be disregarded for present purposes. Only five fully independent experimental studies of the standard molar enthalpy of combustion at 25 °C for methane of (presumed) normal isotopic composition, involving measurements having claimed levels of accuracy and precision appropriate to present considerations, are available in the scientific literature for conversion to the quantities requiring to be listed in ISO 6976:2016.

These five studies are those of Rossini (1931)^[20], of Pittam and Pilcher (1972)^[67], of the OFGEM group (2002)^[68], of Alexandrov (2002)^[69] and, most recently, of the GERG-PTB collaboration (2010)^[70].

The values of the data points, in chronological order, of these five studies are given below in [11.1.2](#) (in $\text{kJ}\cdot\text{mol}^{-1}$ with the negative sign removed).

11.1.2 Selection of data

The data selected for inclusion in the evaluation made in [11.1.4](#) are as listed below (SD = standard deviation, SE = standard error). Notes 1 to 5 refer to various important aspects of these selections. [Figure 4](#) is a histogram, plotted with an interval of 0,2 $\text{kJ}\cdot\text{mol}^{-1}$, of the entire set of 48 data points.

	Rossini revised	Pittam- Pilcher	OFGEM Lythall	OFGEM Dale	Alexandrov	GERG-PTB
	891,823	890,36	890,60	890,34	889,63	890,639
	890,633	891,23	890,69	890,11	890,47	890,459
	890,013	890,62	890,87	890,49	890,85	890,443
	890,503	890,24	890,62	891,34	890,37	890,780
	890,340	890,61	890,81	890,36	890,44	890,568
	890,061	891,17	890,94	890,44	890,79	890,530
			890,71	890,47	890,66	890,597
			890,59	890,87	890,02	890,628
			890,64	890,31		890,562
				890,33		
Mean	890,562	890,705	890,719	890,506	890,404	890,578
SD	0,663	0,411	0,126	0,351	0,408	0,102
SE	0,271	0,168	0,042	0,111	0,144	0,034

NOTE 1 Rossini's values are given in accordance with a re-working by Armstrong and Jobe^[7]. This re-working accounts for revisions that have taken place since 1931 to the International Temperature Scale and to values of molecular mass, etc. An independent and more detailed (unpublished) re-working gives the same final mean value but the individual values differ (see [11.1.3](#)).

NOTE 2 The OFGEM group reported two semi-independent sets of measurements, one made by Lythall and the other by Dale. Thus there are six sets of data, not five, given above.

NOTE 3 The Alexandrov values have been calculated from the mass-basis values given in Reference [69] by using 16,042 46 kg·kmol⁻¹ as the molar mass of methane. The resulting values all differ by 0,03 kJ·mol⁻¹ from those given in Reference [71] (the molar-basis values given by Alexandrov in Reference [71] are recovered if 16,043 is used for the molar mass of methane).

NOTE 4 The provenance of two further sets of values reported by Alexandrov[71] and ascribed by him to GOMB (later subsumed within OFGEM) as GOMB series 1 (9 points) and series 2 (11 points) is not established, and these data are therefore excluded from consideration.

NOTE 5 In the analysis of his own data, Rossini rejected the highest (first) value as a statistical outlier, which gives a revised mean and standard deviation of -890,310 ± 0,271 kJ·mol⁻¹ based on the remaining five data points.

NOTE 6 See 4.4 for elucidation of the acronyms used in this clause.

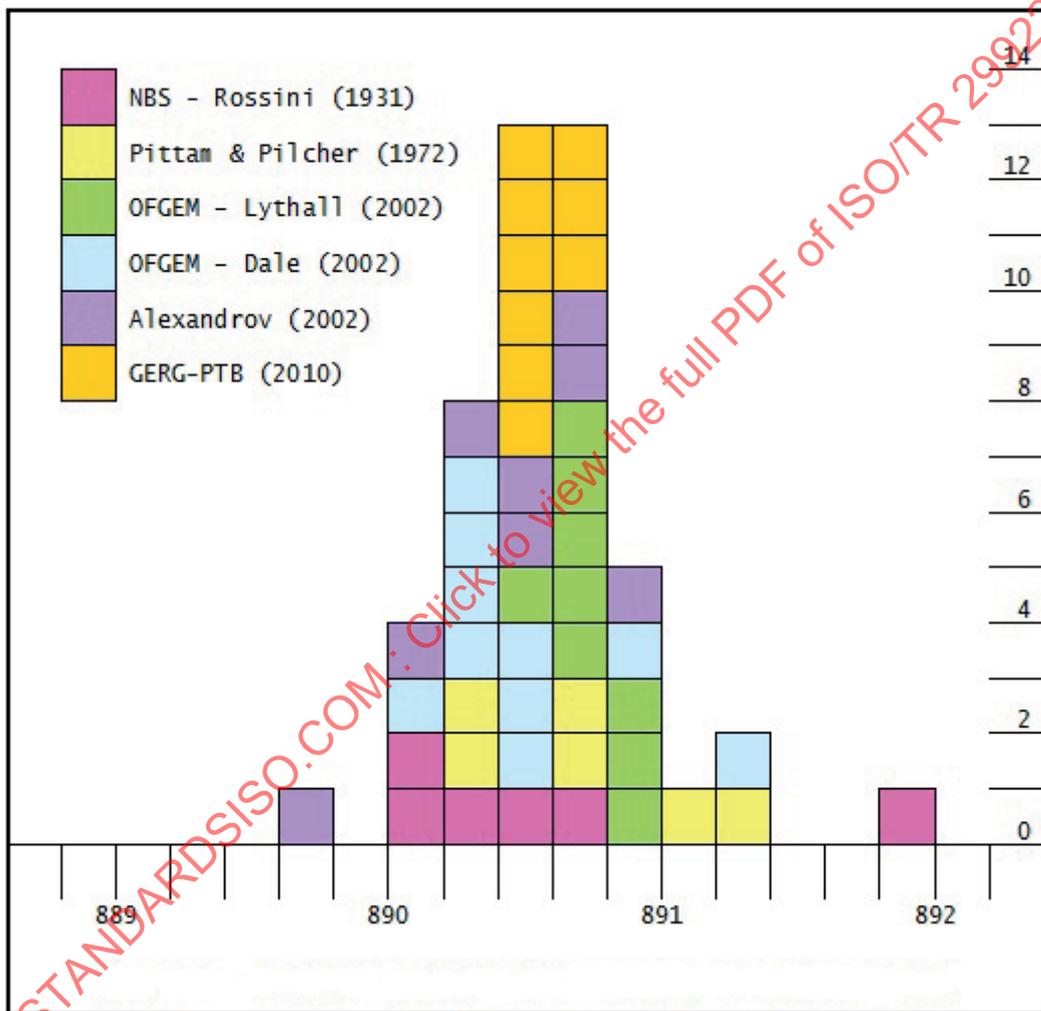


Figure 4 — Standard enthalpy of combustion of methane kJ/mol

11.1.3 Recalculation of Rossini values

In 11.1.2 Note 1, it is mentioned that an alternative (unpublished) treatment of Rossini’s values of the standard enthalpy of combustion $(Hc)_G^0$ of methane gives rise to a set of values which differ individually

from those given by Armstrong and Jobe^[7] but which, remarkably, result in the same mean value. Here is that alternative treatment (negative sign understood throughout).

- a) Original reported values in Int kJ/mol at 30 °C, from *J. Res. NBS* volume 6 (1931) pp. 37-49^[20], in chronological order

891,210

890,020

889,400

889,890

889,727

889,448 mean value 889,949

- b) Values obtained after omitting improper pressure correction, as suggested by Rossini himself in *J. Res. NBS* volume 7 (1931) p. 329^[20]

$891,210 - 0,013 = 891,197$

$890,020 - 0,007 = 890,013$

$889,400 + 0,007 = 889,407$

$889,890 + 0,047 = 889,937$

$889,727 + 0,067 = 889,794$

$889,448 - 0,007 = 889,441$ mean value 889,965

- c) Convert from Int kJ to kJ using factor of 1,000 165 as given by Rossini in *Fundamental Measures and Constants for Science and Technology*, CRC Press, Cleveland, Ohio (1974)^[72], page 82

$891,197 \times (1,000\ 165) = 891,344$

$890,013 \times (1,000\ 165) = 890,160$

$889,407 \times (1,000\ 165) = 889,554$

$889,937 \times (1,000\ 165) = 890,084$

$889,794 \times (1,000\ 165) = 889,941$

$889,441 \times (1,000\ 165) = 889,588$ mean value 890,112

- d) Convert from old molecular weight of water to current value using factor of $(18,015\ 6) \div (18,015\ 28) = 1,000\ 018$ (mass of methane burned was determined by mass of water created)

$891,344 / (1,000\ 018) = 891,328$

$890,160 / (1,000\ 018) = 890,144$

$889,554 / (1,000\ 018) = 889,538$

$890,084 / (1,000\ 018) = 890,068$

$889,941 / (1,000\ 018) = 889,925$

$889,588 / (1,000\ 018) = 889,572$ mean value 890,096

- e) Correct from 30 °C to 25 °C – the best estimate of $[h^o(25) - h^o(30)]$ for the stoichiometric combustion reaction using Cp^o values calculated from the formulation given in Reference [12] is

$$\begin{aligned} [h^o(25) - h^o(30)] &= (30-25) \times \sum v_i \cdot (Cp^o)_i \\ &= 5 \times [0,035\ 8 + 2 \cdot (0,029\ 3) - 0,037\ 0 - 2 \cdot (0,075\ 3)] \\ &= -0,466\ \text{kJ} \cdot \text{mol}^{-1} \text{ for } 5\ \text{°C shift} \end{aligned}$$

$$891,328 + 0,466 = 891,794$$

$$890,144 + 0,466 = 890,610$$

$$889,538 + 0,466 = 890,004$$

$$890,068 + 0,466 = 890,534$$

$$889,925 + 0,466 = 890,391$$

$$889,572 + 0,466 = 890,038 \quad \text{mean value } (890,562 \pm 0,654)\ \text{kJ} \cdot \text{mol}^{-1}$$

[see [Formulae \(2\)](#) and [\(3\)](#) and [5.5](#) example 1 for a similar calculation]

- f) The values given in Armstrong and Jobe[7] were obtained by adding a constant value of $0,613\ \text{kJ} \cdot \text{mol}^{-1}$ to the values given in Rossini's first paper[20]. This constant was supposed to take account of all the various corrections, but no details are given (It seems a little odd that the Rossini original (not revised) values were used as the starting data).

The Armstrong and Jobe values are repeated below:

$$891,210 + 0,613 = 891,823$$

$$890,020 + 0,613 = 890,633$$

$$889,400 + 0,613 = 890,013$$

$$889,890 + 0,613 = 890,503$$

$$889,727 + 0,613 = 890,340$$

$$889,448 + 0,613 = 890,061 \quad \text{mean value } (890,562 \pm 0,663)\ \text{kJ} \cdot \text{mol}^{-1}$$

It is somewhat astonishing that, despite the different approaches, the final mean values are identical (although the standard deviations are not quite the same).

11.1.4 Evaluation of selected data

In making their measurements, each of the later authors, except for Alexandrov, used similar apparatus based upon Rossini's original design. Each in turn, of course, claims improvements in equipment and technique, but there seems to be no clear evidence of improvements in their results, except possibly for the GERG-PTB data. Thus there is reason to treat the results as, in some way, of equal validity. Alexandrov's apparatus differs in principle from the others, but likewise gives results which appear to be of equal validity.

Some of the technical comparisons between the calorimetric methodologies employed in the generation of the various data sets are discussed briefly in [11.3](#).

Notwithstanding the discussion in [11.3](#), however, in none of the source literature for Rossini-type apparatuses is sufficient information given which would allow the estimation of anything like a proper detailed modern uncertainty budget. The OFGEM group come closest; they report[68] a combined standard uncertainty of $0,21\ \text{kJ} \cdot \text{mol}^{-1}$, but the standard deviation of their combined set of results exceeds this value. Alexandrov[69] does make a fairly complete uncertainty analysis for his apparatus;

he suggests a combined relative standard uncertainty of about 0,04 % (0,36 kJ·mol⁻¹). The GERG-PTB collaboration has supported a project to develop a complete and impartial uncertainty budget for their instrument, but no results from this complex study are yet published. An interim estimate made by the group^[70] suggests that the target uncertainty of 0,05 % for each individual measurement has been achieved.

In the end, however, the only sensible way forward seems to be to treat the entire set of results in some statistical fashion. There are (at least) three options.

- a) It can be shown statistically that all the measurements (including Rossini's possible outlier) may be lumped together, without weighting, and considered as part of a single, homogeneous, well-distributed, population (i.e. the distribution is near-normal – see [Figure 4](#)). This allows the calculation of a GUM Type A uncertainty^[62] to accompany the (global) population mean value.

This is essentially the same conclusion as reached previously by Armstrong and Jobel^[71], who themselves discussed several of the technical points listed in [11.3](#), for the (then) two sets of available data.

All the 48 data points may thus be retained and apportioned equal weight. This treatment results in a standard enthalpy of combustion for methane at 25 °C (where the Type A uncertainty is written as one standard deviation) of

$$(Hc)_G^0 = (-890,574 \pm 0,360) \text{ kJ}\cdot\text{mol}^{-1}$$

with two data points, one high (Rossini) and one low (Alexandrov), not within two standard deviations of the experimental mean value. This is the simplest possible statistical treatment of the available measurements. The corresponding experimental standard deviation of the mean (formerly known as the standard error), obtained by dividing the experimental standard deviation by the square-root of the number of data points, is 0,05 kJ·mol⁻¹.

The same result as given by this simple treatment may readily be obtained by application of the more formal analysis-of-variance (ANOVA) methodology (see GUM^[62]) to the case in which all 48 of the data points are taken to be of equal validity.

- b) An alternative approach is, instead of lumping all the data together into one large (48-point) set, to retain the data in their original smaller (6 to 10-point) sets and to take into account the 'individuality' of these sets. This implies the need for an analysis which takes into account both 'between sets' and 'within sets' variations.

The model upon which this approach is based is as follows.

If $(Hc)_{kj}$ is the j -th measurement of Hc in the k -th group of data, where $j = 1$ to n_k (with $n_k = 6$ to 10) and $k = 1$ to m (with $m = 6$), then

$$(Hc)_{kj} = [Hc] + E_k + \lambda_{kj} \quad (72)$$

where

$[Hc]$ is the unknown (target) true value of Hc ;

E_k is the non-random (systematic) bias of $(Hc)_{kj}$ from $[Hc]$ for the k -th group;

λ_{kj} is the random contribution to the measurement $(Hc)_{kj}$.

By definition, the mean (or total) value λ_k of λ_{kj} for the k -th group is zero. Hence, by summation

$$\sum_{j=1}^{n_k} (Hc)_{kj} = n_k \cdot (Hc)_k = n_k \cdot ([Hc] + E_k) \quad (73)$$

where $(Hc)_k$ is the mean value of the group k measurements of Hc .

Hence,

$$(Hc)_k = [Hc] + E_k \tag{74}$$

where the value of E_k is different for each set or group of measurements.

Now, by combining the m groups of measurements,

$$\sum_{k=1}^m (Hc)_k = m \cdot [Hc] + \sum_{k=1}^m E_k \tag{75}$$

or

$$[Hc] = (1/m) \cdot \left(\sum_{k=1}^m [(Hc)_k - E_k] \right) \tag{76}$$

Of course, the values of E_k are unknown (and in principle unknowable) and so, as expected, the true value $[Hc]$ is impossible to evaluate. However, the best estimate of Hc is arguably (though not necessarily) that obtained with the assumption that the sum of the m values of E_k is zero. That, in essence, is the assumption made herein in the evaluation of Hc (redesignated as $(Hc)_G^o$), for the purposes of ISO 6976:2016 and elaborated below, as the mean of the mean values of the $m = 6$ sets of data.

Regardless of whether or not that argument is valid (there are, as also noted below, several other ways in which a defensible estimate of Hc could be made), some further inferences may be made. In particular it may be noted that once each value of $(Hc)_k$ is known, and a resultant value of Hc has been derived (and identified as a pseudo-true or best-estimate value), it is tantamount to having made an estimate (including uncertainty) of each value of E_k .

In respect of the estimation of overall uncertainty in Hc , the essence of the required calculation may be summarized as follows. For each set or group of data there is an uncertainty associated with the mean calculated value $(Hc)_k$ (or, equivalently, with the group bias E_k) of that group and, when using these mean values, there is a further uncertainty associated with the mean-of-means calculated value of Hc . There are, therefore, two types of contribution to the uncertainty. The uncertainty associated with the mean-of-means calculation has here been designated as the ‘between sets’ contribution and the average uncertainty associated with the mean values calculations as the ‘within sets’ contribution (although a better designation for the latter might be the ‘average set-mean’ uncertainty).

In any event, as explained above, if all sets or groups of data (instead of all data points) are treated equally, then a value of $(Hc)_G^o$ may be obtained simply as the mean of the mean values of the six sets. This gives a value of

$$(Hc)_G^o = (-890,57_9 \pm 0,12_0) \text{ kJ} \cdot \text{mol}^{-1}$$

where the value of uncertainty given here, calculated as the standard deviation $(SD)_m$ of the six mean values, may be interpreted as the ‘between sets’ contribution to the total uncertainty, to which the “within sets” uncertainty is to be added.

In terms of its practical result, this approach is not significantly different from simply adopting the most recent value of $(Hc)_G^o$, i.e. the value determined by the GERG-PTB collaboration, as the “best available estimate”.

There is an argument that it is inappropriate to consider each of the six sets of data as of equal validity. However any attempt to weight each set, according either to the number of points in that set or by the inverse of the variance $(1/(SD)_k^2)$ of that set, is open to objection. In the first case the mean value simply reverts to the 48-point mean value calculation (as evaluated above in a)); the second case is discussed under c) below.

The “within sets” contribution that must be added (in quadrature) to the “between sets” uncertainty may be estimated as follows. On the assumption that the uncertainties of individual determinations within a particular group are equal and uncorrelated, then the standard uncertainty of the mean (standard error) for that group is given by $(SE)_k = [(SD)_k / \sqrt{n_k}]$, where n_k is the number of data points in the k -th group ($n_k = 6$ to 10). The root-mean-square average over the m distinct data sets ($m = 6$) of this quantity may then be interpreted as the average ‘within sets’ contribution to the total uncertainty. The value of this quantity is $0,15_1 \text{ kJ}\cdot\text{mol}^{-1}$.

Thus the total standard uncertainty, determined by combining in quadrature the “between sets” and “within sets” contributions may be written as

$$u\left((Hc)_G^o\right) = \sqrt{(SD)_m^2 + \frac{1}{m} \sum_{k=1}^m (SE)_k^2} \quad (77)$$

$$= [(0,120)^2 + (0,151)^2]^{1/2} = 0,193 \text{ kJ}\cdot\text{mol}^{-1}.$$

Thus the final best estimate of the true value and of the standard uncertainty as determined by this second method is

$$(Hc)_G^o = (-890,57_9 \pm 0,19_3) \text{ kJ}\cdot\text{mol}^{-1}$$

- c) A third method for making the required calculation is similar in most respects to option b) except that, instead of taking each set of data to have equal weight, each set is weighted according to the inverse of the variance $(SD)_k^2$ of that set. The mean value for $(Hc)_G^o$ is then obtained as

$$(Hc)_G^o = \sum_{k=1}^m (Hc)_k / (SD)_k^2 / \sum_{k=1}^m 1 / (SD)_k^2 \quad (78)$$

The value of $(Hc)_G^o$ obtained from this calculation is $890,62_2 \text{ kJ}\cdot\text{mol}^{-1}$ and the ‘between groups’ uncertainty, obtained as the standard deviation about this mean value is $0,12_9 \text{ kJ}\cdot\text{mol}^{-1}$. The ‘within groups’ uncertainty is unchanged at $0,15_1 \text{ kJ}\cdot\text{mol}^{-1}$. Combination of these values in quadrature results in an estimated standard uncertainty of $0,19_9 \text{ kJ}\cdot\text{mol}^{-1}$. Thus the final best estimate obtained by this method is

$$(Hc)_G^o = (-890,62_2 \pm 0,19_9) \text{ kJ}\cdot\text{mol}^{-1}$$

Of these three alternative schemes, method b) has been selected as technically superior. It seems clear (by simple observation of the data) that the value of uncertainty obtained by method a) is too high – in other words it is not valid in the present application to interpret the standard deviation of the entire population of 48 points as a reasonable measure of the standard uncertainty. In respect of method c), it is readily seen that the result places much emphasis on the two sets of data with the lowest spread of data points (OFGEM-Lythall and GERG-PTB). This level of emphasis, however, seems unwarranted in the sense that it is unsupported by any insightful technical reasoning; moreover, the mean values of these two sets of data are offset from each other by an amount slightly greater than the standard deviation of either set and, therefore, the two sets are only marginally consistent with each other.

The assumption used in option b) that the sum of the m values of E_k is zero may, of course, be invalid. In this case it implies that some non-random contributions to the uncertainty remain unaccounted for by the analysis presented above. However the fact that the distribution of all the results appears close to normal suggests that any such non-random components would need to be about equally applicable to all the sets of data, which seems unlikely. Nevertheless it cannot be certain that no non-random effects remain, and indeed the authors of the GERG-PTB set of data implicitly acknowledge this possibility by quoting an estimate of their single-point measurement uncertainty that substantially exceeds the overall spread of their collected results. In this sense the value adopted for $u((Hc)_G^o)$ of $0,19 \text{ kJ}\cdot\text{mol}^{-1}$ is

arguably something of an underestimate but, because there appears to be no way to quantify the extent of any underestimation, this value is retained as the best estimate for the purposes of ISO 6976:2016.

11.1.5 Selected value and uncertainty

For the purposes of ISO 6976:2016 the values given by method b) have been rounded so as to give a final value of

$$(Hc)_G^o = (-890,58 \pm 0,19) \text{ kJ} \cdot \text{mol}^{-1}$$

11.2 Derived calorific values

For convenience, given below, in [Tables 10](#) to [12](#), is a self-consistent set of calorific values for methane for all of the reference conditions considered in ISO 6976:2016. In this set, a tiny enthalpic correction (residual enthalpy) of 0,01 kJ·mol⁻¹ has been applied to convert the ideal-gas enthalpy of combustion to the real-gas enthalpy of combustion. This correction is so small that it is justifiably ignored for the purposes of the calculations prescribed in ISO 6976:2016, but is included here for completeness in the special case of pure methane. For further explanation, see [Clause 6](#).

Table 10 — Calorific value of methane on a molar basis

(95 % confidence limit of approximately ±0,40 kJ·mol⁻¹)

ideal gross at 25 °C	890,58 kJ·mol ⁻¹
real gross at 25 °C	890,59 kJ·mol ⁻¹
ideal gross at 20 °C	891,05 kJ·mol ⁻¹
real gross at 20 °C	891,06 kJ·mol ⁻¹
ideal gross at 15 °C	891,51 kJ·mol ⁻¹
real gross at 15 °C	891,52 kJ·mol ⁻¹
ideal gross at 0 °C	892,92 kJ·mol ⁻¹
real gross at 0 °C	892,93 kJ·mol ⁻¹
ideal gross at 60 °F	891,46 kJ·mol ⁻¹ (383 259 Btu _{IT} ·lb-mol ⁻¹)
real gross at 60 °F	891,47 kJ·mol ⁻¹ (383 263 Btu _{IT} ·lb-mol ⁻¹)
ideal net at 25 °C	802,55 kJ·mol ⁻¹
real net at 25 °C	802,56 kJ·mol ⁻¹
ideal net at 20 °C	802,61 kJ·mol ⁻¹
real net at 20 °C	802,62 kJ·mol ⁻¹
ideal net at 15 °C	802,65 kJ·mol ⁻¹
real net at 15 °C	802,66 kJ·mol ⁻¹
ideal net at 0 °C	802,79 kJ·mol ⁻¹
real net at 0 °C	802,80 kJ·mol ⁻¹
ideal net at 60 °F	802,64 kJ·mol ⁻¹ (345 073 Btu _{IT} ·lb-mol ⁻¹)
real net at 60 °F	802,65 kJ·mol ⁻¹ (345 077 Btu _{IT} ·lb-mol ⁻¹)

Table 11 — Calorific value of methane on a mass basis(95 % confidence limit of approximately $\pm 0,025 \text{ MJ}\cdot\text{kg}^{-1}$)

ideal gross at 25 °C	55,514 MJ·kg ⁻¹
real gross at 25 °C	55,515 MJ·kg ⁻¹
ideal gross at 20 °C	55,543 MJ·kg ⁻¹
real gross at 20 °C	55,544 MJ·kg ⁻¹
ideal gross at 15 °C	55,572 MJ·kg ⁻¹
real gross at 15 °C	55,573 MJ·kg ⁻¹
ideal gross at 0 °C	55,660 MJ·kg ⁻¹
real gross at 0 °C	55,660 MJ·kg ⁻¹
ideal gross at 60 °F	55,569 MJ·kg ⁻¹ (23 890 Btu _{IT} ·lb ⁻¹)
real gross at 60 °F	55,569 MJ·kg ⁻¹ (23 890 Btu _{IT} ·lb ⁻¹)
ideal net at 25 °C	50,027 MJ·kg ⁻¹
real net at 25 °C	50,027 MJ·kg ⁻¹
ideal net at 20 °C	50,030 MJ·kg ⁻¹
real net at 20 °C	50,031 MJ·kg ⁻¹
ideal net at 15 °C	50,033 MJ·kg ⁻¹
real net at 15 °C	50,033 MJ·kg ⁻¹
ideal net at 0 °C	50,042 MJ·kg ⁻¹
real net at 0 °C	50,042 MJ·kg ⁻¹
ideal net at 60 °F	50,032 MJ·kg ⁻¹ (215 10 Btu _{IT} ·lb ⁻¹)
real net at 60 °F	50,033 MJ·kg ⁻¹ (215 10 Btu _{IT} ·lb ⁻¹)

Table 12 — Calorific value of methane on a volume basis at $p_0 = 101,325$ kPa(95 % confidence limit of approximately $\pm 0,018$ MJ·m⁻³)

ideal gas, gross, combustion at 25 °C and metering at 0 °C	39,733 MJ·m ⁻³
ideal gas gross combustion 15 °C metering 0 °C	39,775 MJ·m ⁻³
ideal gas gross combustion 15 °C metering 15 °C	37,704 MJ·m ⁻³
ideal gas gross combustion 0 °C metering 0 °C	39,838 MJ·m ⁻³
ideal gas gross combustion 20 °C metering 20 °C	37,042 MJ·m ⁻³
ideal gas gross combustion 25 °C metering 20 °C	37,022 MJ·m ⁻³
ideal gas gross combustion 60 °F metering 60 °F	37,630 MJ·m ⁻³ (1 009,9 Btu _{IT} ·ft ⁻³)
ideal gas net combustion 25 °C metering 0 °C	35,806 MJ·m ⁻³
ideal gas net combustion 15 °C metering 0 °C	35,810 MJ·m ⁻³
ideal gas net combustion 15 °C metering 15 °C	33,946 MJ·m ⁻³
ideal gas net combustion 0 °C metering 0 °C	35,817 MJ·m ⁻³
ideal gas net combustion 20 °C metering 20 °C	33,365 MJ·m ⁻³
ideal gas net combustion 25 °C metering 20 °C	33,363 MJ·m ⁻³
ideal gas net combustion 60 °F metering 60 °F	33,881 MJ·m ⁻³ (909,3 Btu _{IT} ·ft ⁻³)
real gas gross combustion 25 °C metering 0 °C	39,829 MJ·m ⁻³
real gas gross combustion 15 °C metering 0 °C	39,870 MJ·m ⁻³
real gas gross combustion 15 °C metering 15 °C	37,780 MJ·m ⁻³
real gas gross combustion 0 °C metering 0 °C	39,933 MJ·m ⁻³
real gas gross combustion 20 °C metering 20 °C	37,112 MJ·m ⁻³
real gas gross combustion 25 °C metering 20 °C	37,092 MJ·m ⁻³
real gas gross combustion 60 °F metering 60 °F	37,704 MJ·m ⁻³ (1 011,9 Btu _{IT} ·ft ⁻³)
real gas net combustion 25 °C metering 0 °C	35,892 MJ·m ⁻³
real gas net combustion 15 °C metering 0 °C	35,896 MJ·m ⁻³
real gas net combustion 15 °C metering 15 °C	34,014 MJ·m ⁻³
real gas net combustion 0 °C metering 0 °C	35,903 MJ·m ⁻³
real gas net combustion 20 °C metering 20 °C	33,428 MJ·m ⁻³
real gas net combustion 25 °C metering 20 °C	33,426 MJ·m ⁻³
real gas net combustion 60 °F metering 60 °F	33,948 MJ·m ⁻³ (911,1 Btu _{IT} ·ft ⁻³)

11.3 Comparisons between calorimetric methodologies

This subclause discusses, in outline rather than in detail, some of the technical distinctions between the equipment and techniques used in sequence by Rossini (1931), by Pittam and Pilcher (1972), by the OFGEM group (2002), by Alexandrov (2002) and by the GERG-PTB collaboration (2010) in their respective determinations of the standard enthalpy of combustion of methane. For a more detailed consideration of the design issues involved in the development of this kind of instrument, including an intricate – but preliminary – discussion of uncertainty issues, see the report by Pramann[73].

NOTE In the case of the OFGEM and GERG-PTB groups' measurements, not all of the relevant experimental details can be retrieved from their publications[68][70]. Some of these details have therefore been obtained by direct private contact with the authors[110]. Of course, this is not to say that sufficient detail is always given in the publication(s) of the other groups, but in these cases there is no easy recourse to private contact.

a) Impurities

The methane sample used by Rossini had a measured impurity level of 1 210 ppm carbon monoxide, for which a correction was made, while Pittam and Pilcher used a sample containing less than 5 ppm impurities. The OFGEM group used modern commercially-available ultra-high purity methane which was checked by analysis to contain less than 5 ppm impurities. Alexandrov does not mention purity and so, presumably, used samples of sufficiently high purity that this was not seen as an issue. The GERG-PTB study used methane with impurities of up to 50 ppm, checked by analysis at the Bundesanstalt für Materialforschung und Prüfung (BAM).

b) Isotopic distribution

None of the authors makes any claim that the sample of methane used in their measurements is of normal isotopic distribution, although it is presumably to be inferred that this is so. Nor does any author indicate the method by which their sample has been prepared (perhaps by a commercial supplier) and purified. It does, however, seem possible that some production processes (e.g. any involving fractionation) might have the potential to disturb the normal (terrestrial) isotopic distribution of the product. This could result in either depletion or enrichment of the normal carbon-13 concentration of 1,11 %. Any such variation would clearly have a direct and predictable effect on the molar mass of the sample, but it is not clear what – if any – other effect this might have on the measured heat of combustion.

c) Calibration and traceability

Rossini calibrated his calorimeter using an electrical heating method, with traceability to measurement standards maintained at the U.S. National Bureau of Standards (NBS-Gaithersburg). Pittam and Pilcher used the standard enthalpy of combustion of hydrogen for calibration purposes, with traceability thereby only to Rossini's earlier work on the combustion of hydrogen^[18]. The OFGEM group used an electrical calibration method in which the calibration of all constituent measurement equipment was traceable to national standards held by the U.K. National Physical Laboratory (NPL-Teddington), except for the timing element which was derived from and traceable to BBC standard time signals. In similar fashion, the GERG-PTB group used an electrical calibration method in which the calibration of all constituent measurement equipment was traceable to German national standards held on site at the Physikalisch-Technische Bundesanstalt (PTB-Braunschweig) where the calorimeter facility was at that time installed.

d) Temperature measurement

Rossini made temperature readings every minute in the most critical parts of both calibration and combustion experiments; Pittam and Pilcher, every 30 s; and the OFGEM group (the first to use computer-assisted data collection), every three seconds. In each case the measurements were made using platinum resistance thermometry, but only in Rossini's work at NBS was it possible to have in-house traceability to national standards. The OFGEM platinum resistance thermometers were calibrated at NPL and checked internally from time to time using a certified triple-point of water cell. The GERG-PTB collaboration made temperature measurements every two seconds using a thermistor calibrated *in situ* against a traceable platinum resistance thermometer. The lower response time achieved using this arrangement allows rapid temperature changes in the heat exchange fluid to be followed more closely. The GERG-PTB group also made the only (reported) investigation to date^[74] of the dynamic temperature distribution within the heat exchange fluid, in particular of the difference in temperature profile between calibration (where the electrical heating energy input is spatially non-localized) and combustion experiments (where the heat energy input from the flame is much more localized).

e) Mass determination

In order to determine the mass of gas burnt in a combustion run, Rossini measured the amount of water formed, the standard method at that time, while Pittam and Pilcher measured the amount of carbon dioxide formed, the method preferred at that later time. The OFGEM group determined the amount of gas burnt by direct before-and-after weighing of the sample bottle, using mass pieces calibrated by a UKAS-NAMAS-accredited trading standards laboratory. The GERG-PTB group determined the

amount of gas burnt by direct weighing, using a fully automated system with traceability back to the international standard of mass.

f) Ignition energy

Rossini conducted separate “blank” experiments designed to determine directly the amount of energy input from his spark-ignition source. Pittam and Pilcher, and the OFGEM group, both made long and short combustion runs by means of which, by subtraction, the spark-ignition energy was deemed to be eliminated from further consideration. The GERG-PTB group made a direct experimental *in situ* determination of the ignition energy, and simply subtracted the value obtained from the uncorrected results.

g) Unburnt gas

The GERG-PTB group determined the small amount of gas left unburnt (or incompletely burnt) at the start (ignition) and/or finish (extinction) of a combustion run by using quantitative infrared detection. All the other groups appear to have used the “subtraction” method of long and short runs in order to preclude the need for further consideration of this issue.

h) Calorimeter integrity and re-assembly

Rossini re-assembled his calorimeter prior to each experiment, filling the heat-exchange water jacket each time with a weighed amount of water, and using oil films to “seal” the instrument for each individual experiment. He then referred his calibration and combustion to a standard mass of water. Pittam and Pilcher calibrated their calorimeter over a series of experiments and then used that energy equivalent throughout their work. They claim to have “sealed” the heat-exchange water into their calorimeter for the duration of the test series but, in fact, removed a platinum resistance thermometer after each experiment and replaced it with a mercury thermoregulator, with the consequent possibility of water loss. Even after the calorimeter had been dismantled, modified and re-assembled, they continued to use the same energy equivalent, the justification for this apparently being the same mass of water used to re-fill the water jacket. The OFGEM calorimeter was permanently sealed for the duration of a test series, the energy equivalent of the assembly being remeasured regularly to verify the absence of any drift or other change. For the GERG-PTB study the calorimeter was also permanently sealed, with calibrations and measurements being carried out in an alternating sequence during the test series.

i) Alkane series enthalpies of formation

The regular progression of the enthalpies of formation of the lower n-alkane homologous series, each of which adds a further CH₂ increment to the previous member of the series, has been claimed^[Z] slightly to favour the enthalpy of combustion of methane obtained by Pittam and Pilcher over that of Rossini, or may perhaps suggest a value somewhere between these two earliest studies. Because, however, methane is in a unique position at the extreme lower end of the series, such an argument does not seem to carry much conviction. Nevertheless, the overall mean value of the six studies now available does indeed suggest a value between the Rossini and Pittam-Pilcher values, but is much closer to the Rossini value.

12 Calorific values on a mass basis

12.1 Calorific values on a mass basis for components of natural gas

Table 13 gives the ideal-gas mass-basis gross calorific values for the complete set of likely components of a fuel gas mixture for five combustion reference temperatures, $t_1 = 25\text{ °C}$, 20 °C , $15,55\text{ °C}$ (60 °F), 15 °C and 0 °C . Each of the values has been obtained by dividing the appropriate value of $[(Hc)_G^0]_j(t_1)$ from ISO 6976:2016, Table 3 by the corresponding molar mass M_j from ISO 6976:2016, Table 1 and rounding to two places of decimal (except for methane).

It is stressed that [Table 13](#) is provided only on an informative basis i.e. the values given may not be used in normative applications of ISO 6976:2016.

NOTE The non-zero calorific value of water vapour derives formally from the definition of gross calorific value, which requires condensation to the liquid state of all water vapour in the products of combustion. Thus any water vapour present in an otherwise dry gas contributes its latent heat of vaporization to the gross calorific value of the mixture. For a fuller explanation, see [Clause 10](#).

12.2 Alternative (non-normative) method of calculation for mass-basis calorific values

Use of Formulae (4) and (5) in ISO 6976:2016, Clause 8 represents the definitive method for calculating $(Hm)_G^o(t_1)$. An alternative (non-normative) method is by use of

$$(Hm)_G^o(t_1) = \sum_{j=1}^N \left(x_j \cdot \frac{M_j}{M} \cdot [(Hm)_G^o]_j(t_1) \right) \quad (79)$$

where

$[(Hm)_G^o]_j(t_1)$ is the ideal-gas mass-basis gross calorific value of component j , of molar mass M_j , as given in [Table 13](#);

x_j is the mole fraction of component j ;

N is the number of components in the mixture;

M is the molar mass of the mixture, calculated in accordance with ISO 6976:2016, Formula (5).

Numerical values obtained from this method will normally be concordant to within 0,01 MJ·kg⁻¹ of values calculated by the definitive method given in ISO 6976:2016, which is within the limits of uncertainty and significance for the current state-of-the-art.

The extension of this alternative non-normative method to the calculation of mass-basis net calorific values is straightforward and will not be elaborated here.

Table 13 — Gross calorific values for components of natural gases at various combustion reference temperatures for the ideal gas on a mass basis

<i>j</i>	component	Ideal-gas mass-basis gross calorific value $(Hm)_C^o$ [MJ·kg ⁻¹ , (Btu _{IT} ·lb ⁻¹)				
		0 °C	15 °C	15,55 °C (60 °F)	20 °C	25 °C
1	methane	55,660	55,572	55,569 (23 890)	55,543	55,514
2	ethane	52,03	51,95	51,95 (22 334)	51,93	51,90
3	propane	50,44	50,37	50,37 (21 654)	50,35	50,33
4	n-butane	49,61	49,55	49,54 (21 300)	49,53	49,51
5	2-methylpropane	49,45	49,39	49,39 (21 232)	49,37	49,35
6	n-pentane	49,11	49,05	49,04 (21 085)	49,03	49,01
7	2-methylbutane	49,01	48,95	48,95 (21 044)	48,93	48,91
8	2,2-dimethylpropane	48,81	48,75	48,75 (20 959)	48,73	48,71
9	n-hexane	48,78	48,72	48,72 (20 944)	48,70	48,68
10	2-methylpentane	48,69	48,63	48,63 (20 906)	48,61	48,59
11	3-methylpentane	48,72	48,66	48,66 (20 919)	48,64	48,62
12	2,2-dimethylbutane	48,57	48,52	48,51 (20 857)	48,50	48,48
13	2,3-dimethylbutane	48,66	48,61	48,60 (20 896)	48,59	48,57
14	n-heptane	48,53	48,47	48,47 (20 839)	48,46	48,44
15	n-octane	48,35	48,29	48,29 (20 760)	48,27	48,25
16	n-nonane	48,21	48,15	48,15 (20 701)	48,13	48,12
17	n-decane	48,09	48,04	48,04 (20 652)	48,02	48,00
56	n-undecane	48,00	47,94	47,94 (20 610)	47,92	47,91
57	n-dodecane	47,92	47,87	47,86 (20 578)	47,85	47,83
58	n-tridecane	47,85	47,80	47,80 (20 548)	47,78	47,76
59	n-tetradecane	47,79	47,74	47,74 (20 524)	47,72	47,71
60	n-pentadecane	47,74	47,69	47,69 (20 503)	47,67	47,66
18	ethene	50,39	50,34	50,34 (21 640)	50,32	50,30
19	propene	48,99	48,94	48,94 (21 040)	48,92	48,91
20	1-butene	48,51	48,46	48,45 (20 832)	48,44	48,42
21	cis-2-butene	48,39	48,34	48,33 (20 780)	48,32	48,30
22	trans-2-butene	48,32	48,27	48,27 (20 752)	48,25	48,24

Table 13 (continued)

<i>j</i>	component	Ideal-gas mass-basis gross calorific value (H_m) ^o MJ·kg ⁻¹ ·(Btu _{IT} ·lb ⁻¹)					
		0 °C	15 °C	15,55 °C (60 °F)	20 °C	25 °C	
23	2-methylpropene	48,21	48,16	48,16 (20 704)	48,14	48,13	
24	1-pentene	48,21	48,16	48,16 (20 705)	48,15	48,13	
25	propadiene	48,55	48,52	48,52 (20 860)	48,51	48,50	
26	1,2-butadiene	48,01	47,98	47,98 (20 626)	47,97	47,95	
27	1,3-butadiene	47,03	47,00	47,00 (20 205)	46,99	46,97	
28	ethyne	50,00	49,98	49,98 (21 488)	49,97	49,97	
29	cyclopentane	47,43	47,37	47,37 (20 365)	47,35	47,33	
30	methylcyclopentane	47,26	47,20	47,20 (20 292)	47,18	47,17	
31	ethylcyclopentane	47,23	47,18	47,17 (20 281)	47,16	47,14	
32	cyclohexane	47,06	47,01	47,00 (20 208)	46,99	46,97	
33	methylcyclohexane	46,94	46,89	46,89 (20 159)	46,87	46,86	
34	ethylcyclohexane	46,99	46,94	46,93 (20 178)	46,92	46,90	
35	benzene	42,31	42,28	42,28 (18 178)	42,27	42,27	
36	toluene	42,90	42,87	42,87 (18 430)	42,86	42,85	
37	ethylbenzene	43,45	43,42	43,42 (18 666)	43,41	43,40	
38	o-xylene	43,35	43,32	43,31 (18 622)	43,31	43,29	
39	methanol	23,92	23,88	23,88 (10 265)	23,86	23,85	
40	methanethiol	25,81	25,78	25,78 (11 084)	25,77	25,76	
41	hydrogen	142,19	141,95	141,94 (61 022)	141,87	141,79	
42	water (see Note)	2,50	2,47	2,47 (1 060)	2,45	2,44	
43	hydrogen sulfide	16,52	16,50	16,50 (7 094)	16,50	16,49	
44	ammonia	22,58	22,52	22,52 (9 680)	22,50	22,48	
45	hydrogen cyanide	24,86	24,85	24,85 (10 685)	24,85	24,85	
46	carbon monoxide	10,10	10,10	10,10 (4 342)	10,10	10,10	
47	carbonyl sulfide	9,12	9,12	9,12 (3 923)	9,13	9,13	
48	carbon disulfide	14,50	14,50	14,50 (6 236)	14,50	14,51	

13 Calorific values on a volume basis

13.1 Calorific values on a volume basis for components of natural gas

[Table 14](#) gives the ideal-gas volume-basis gross calorific values for the complete set of likely components of a fuel gas mixture for seven sets of combustion/metering reference temperatures, $t_1/t_2 = 15/15$ °C, $0/0$ °C, $15/0$ °C, $25/0$ °C, $20/20$ °C, $25/20$ °C and $60/60$ °F. Each of the values has been obtained by multiplying the appropriate value of $[(Hc)_G^o]_j(t_1)$ from ISO 6976:2016, Table 3 by $p_2/R \cdot T_2$, where p_2 is the metering reference pressure and $R (= 8,314\ 462\ 1\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ is the molar gas constant, and rounding to two places of decimal (except for methane and hydrogen).

It is stressed that [Table 14](#) is provided only on an informative basis i.e. the values given may not be used in normative applications of ISO 6976:2016.

NOTE 1 The reference pressure for both combustion and metering is 101,325 kPa in all cases.

NOTE 2 Column headings t_1/t_2 °C refer to the reference temperatures for combustion and metering respectively.

NOTE 3 The non-zero calorific value of water vapour derives formally from the definition of gross calorific value, which requires condensation to the liquid state of all water vapour in the products of combustion. Thus any water vapour present in an otherwise dry gas contributes its latent heat of vaporization to the gross calorific value of the mixture. For a fuller explanation, see [Clause 10](#).

13.2 Alternative (non-normative) method of calculation for volume-basis calorific values

Use of Formulae (7) and (8) in ISO 6976:2016, Clause 9 represents the definitive method for calculating $(Hv)_G^o(t_1;t_2,p_2)$. An alternative (non-normative) method is by use of

$$(Hv)_G^o(t_1;t_2,p_2) = \sum_{j=1}^N x_j \left[(Hv)_G^o \right]_j(t_1;t_2,p_2) \quad (80)$$

where

$\left[(Hv)_G^o \right]_j(t_1;t_2,p_2)$ is the ideal-gas volume-basis gross calorific value of component j , as given in [Table 14](#);

x_j is the mole fraction of component j ;

N is the number of components in the mixture.

Numerical values obtained from this method will normally be concordant to within $0,01\ \text{MJ} \cdot \text{m}^{-3}$ of values calculated by the definitive method given in ISO 6976:2016, which is within the usual limits of uncertainty and significance for the current state-of-the-art.

The extension of this alternative non-normative method to the calculation of ideal-gas volume-basis net calorific values is straightforward and will not be elaborated here.

Further extension to the calculation of real-gas volume-basis calorific values, either gross or net, may be readily achieved by division of the appropriate ideal-gas value by the mixture compression factor $Z(t_2,p_2)$, and likewise will not be elaborated here.

Table 14 — Gross calorific values for components of natural gases at various combustion/metering reference temperatures for the ideal gas on a volume basis

j	component	Ideal-gas volume-basis gross calorific value $\left[\frac{(Hv)_G^0}{G} \right]_j$ MJ·m ⁻³ ·(Btu _{IT} ·ft ⁻³)									
		15/15 °C	0/0 °C	15/0 °C	25/0 °C	20/20 °C	25/20 °C	60/60 °F			
1	methane	37,704	39,838	39,775	39,733	37,042	37,022	37,630 (1 009,9)			
2	ethane	66,07	69,79	69,69	69,63	64,91	64,88	65,94 (1 769,7)			
3	propane	93,94	99,23	99,09	99,01	92,29	92,25	93,75 (2 516,2)			
4	n-butane	121,79	128,64	128,48	128,38	119,67	119,62	121,55 (3 262,4)			
5	2-methylpropane	121,40	128,23	128,07	127,96	119,28	119,23	121,16 (3 252,0)			
6	n-pentane	149,66	158,07	157,87	157,75	147,04	146,99	149,36 (4 008,8)			
7	2-methylbutane	149,36	157,76	157,57	157,44	146,76	146,70	149,07 (4 000,9)			
8	2,2-dimethylpropane	148,76	157,12	156,93	156,80	146,16	146,11	148,47 (3 984,8)			
9	n-hexane	177,55	187,53	187,30	187,16	174,46	174,39	177,20 (4 756,0)			
10	2-methylpentane	177,23	187,19	186,96	186,82	174,14	174,07	176,88 (4 747,4)			
11	3-methylpentane	177,34	187,31	187,08	186,93	174,25	174,18	176,99 (4 750,4)			
12	2,2-dimethylbutane	176,82	186,75	186,53	186,38	173,73	173,66	176,47 (4 736,3)			
13	2,3-dimethylbutane	177,15	187,10	186,87	186,73	174,06	173,99	176,80 (4 745,1)			
14	n-heptane	205,42	216,96	216,70	216,54	201,84	201,76	205,02 (5 502,5)			
15	n-octane	233,29	246,38	246,10	245,91	229,22	229,13	232,83 (6 248,9)			
16	n-nonane	261,19	275,85	275,53	275,33	256,64	256,54	260,68 (6 996,3)			
17	n-decane	289,07	305,29	304,94	304,71	284,03	283,92	288,50 (7 743,0)			
56	n-undecane	316,93	334,71	334,33	334,08	311,41	311,29	316,31 (8 489,4)			
57	n-dodecane	344,82	364,17	363,76	363,49	338,81	338,69	344,14 (9 236,5)			
58	n-tridecane	372,68	393,59	393,15	392,86	366,19	366,05	371,95 (9 982,8)			
59	n-tetradecane	400,56	423,03	422,55	422,24	393,58	393,44	399,77 (10 729,5)			
60	n-pentadecane	428,43	452,47	451,96	451,63	420,97	420,82	427,59 (11 476,2)			
18	ethene	59,72	63,07	63,00	62,96	58,68	58,66	59,61 (1 599,8)			
19	propene	87,10	91,98	91,88	91,82	85,58	85,55	86,93 (2 333,1)			
20	1-butene	114,98	121,42	121,30	121,21	112,98	112,94	114,76 (3 079,9)			
21	cis-2-butene	114,69	121,12	120,99	120,91	112,70	112,66	114,47 (3 072,3)			

Table 14 (continued)

j	component	Ideal-gas volume-basis gross calorific value $\left[\left(\frac{H_v}{G} \right)_G^o \right]_j$ MJ·m ⁻³ ·(Btu _{IT} ·ft ⁻³)							
		15/15 °C	0/0 °C	15/0 °C	25/0 °C	20/20 °C	25/20 °C	60/60 °F	
22	trans-2-butene	114,54	120,96	120,83	120,75	112,55	112,51	114,31 (3 068,1)	
23	2-methylpropene	114,28	120,68	120,55	120,47	112,29	112,25	114,05 (3 061,1)	
24	1-pentene	142,85	150,86	150,70	150,59	140,37	140,32	142,57 (3 826,6)	
25	propadiene	82,22	86,79	86,73	86,69	80,80	80,78	82,06 (2 202,3)	
26	1,2-butadiene	109,75	115,87	115,78	115,72	107,85	107,83	109,54 (2 940,0)	
27	1,3-butadiene	107,51	113,51	113,42	113,36	105,65	105,62	107,30 (2 879,9)	
28	ethyne	55,04	58,08	58,06	58,05	54,09	54,09	54,93 (1 474,3)	
29	cyclopentane	140,50	148,40	148,22	148,10	138,05	138,00	140,23 (3 763,6)	
30	methylcyclopentane	168,01	177,44	177,23	177,10	165,08	165,01	167,67 (4 500,3)	
31	ethylcyclopentane	195,90	206,89	206,65	206,50	192,48	192,41	195,51 (5 247,4)	
32	cyclohexane	167,31	176,71	176,50	176,36	164,39	164,33	166,98 (4 481,6)	
33	methylcyclohexane	194,72	205,65	205,41	205,26	191,33	191,25	194,34 (5 215,8)	
34	ethylcyclohexane	222,75	235,24	234,98	234,81	218,87	218,79	222,31 (5 966,7)	
35	benzene	139,69	147,46	147,36	147,29	137,27	137,24	139,42 (3 741,8)	
36	toluene	167,05	176,35	176,22	176,14	164,16	164,12	166,72 (4 474,7)	
37	ethylbenzene	194,95	205,82	205,65	205,55	191,57	191,52	194,57 (5 222,1)	
38	o-xylene	194,49	205,33	205,17	205,06	191,12	191,07	194,11 (5 209,7)	
39	methanol	32,36	34,20	34,13	34,09	31,78	31,76	32,29 (866,7)	
40	methanethiol	52,45	55,40	55,34	55,30	51,54	51,52	52,35 (1 405,1)	
41	hydrogen	12,102	12,788	12,767	12,752	11,889	11,882	12,078 (324,2)	
42	water (see Note 3)	1,88	2,01	1,98	1,96	1,84	1,83	1,87 (50,3)	
43	hydrogen sulfide	23,78	25,12	25,09	25,07	23,37	23,36	23,74 (637,1)	
44	ammonia	16,22	17,16	17,11	17,08	15,93	15,91	16,19 (434,4)	
45	hydrogen cyanide	28,41	29,98	29,97	29,96	27,92	27,91	28,35 (760,9)	
46	carbon monoxide	11,96	12,62	12,62	12,63	11,76	11,76	11,94 (320,5)	
47	carbonyl sulfide	23,18	24,45	24,46	24,46	22,79	22,79	23,14 (621,0)	
48	carbon disulfide	46,70	49,26	49,27	49,28	45,91	45,91	46,61 (1 251,1)	

14 Approximate conversion between reference conditions

14.1 Factors for conversion between metric reference conditions

Tables 15 to 17 provide a set of conversion factors that enable the conversion of any property for which ISO 6976:2016 prescribes a method of calculation, from any one set of the commonly-used metric reference conditions to any other. The tables are identical to those given in ISO 13443:1996 Natural gas – Standard reference conditions^[25] (except for the addition of net Wobbe index), but are repeated here for the convenience of the user. In addition, Notes 1 and 2 provide further information, including an explanation of the provenance of the tables, that is not given in ISO 13443.

To obtain the value of a property at the reference condition given in row b) from a known value in the same units at the reference condition given in row a), multiply by the factor indicated. To carry out the reverse conversion, divide by the factor indicated. Conversions for properties of the ideal gas are expected to be accurate within $\pm 0,01$ % for all methane-rich natural gas compositions. For the real gas volumetric properties (compression factor, density, relative density) the expected accuracy is $\pm 0,02$ %, and for the real gas combustion properties (calorific values, Wobbe index) $\pm 0,1$ %.

NOTE 1 The conversion factors listed have been calculated from the corresponding property values for pure methane. In consequence they are, to the number of decimal digits given, essentially exact for pure methane. For other natural gases, the conversion factors are not exact but are expected still to be accurate to within the uncertainties quoted above. For very accurate or specific (e.g. contractual) applications, users need to consider the calculation and adoption of specific conversion factors.

NOTE 2 Conversion between reference states cannot result in a value of a property of greater (implied) precision than the value from which it was calculated. Converted values can therefore not be quoted to a greater number of decimal digits than the source values.

Table 15 — Conversion factors for densities, relative densities and compression factor

	a) b)	Metering ($t_2/^\circ\text{C}$)		
		20 to 15	20 to 0	15 to 0
ideal density		1,017 4	1,073 2	1,054 9
ideal relative density		1,000 0	1,000 0	1,000 0
compression factor		0,999 9	0,999 5	0,999 6
real density		1,017 5	1,073 8	1,055 3
real relative density		1,000 1	1,000 3	1,000 2

Table 16 — Conversion factors for molar and mass-basis calorific values

	a) b)	Combustion ($t_1/^\circ\text{C}$)					
		25 to 20	25 to 15	25 to 0	20 to 15	20 to 0	15 to 0
gross calorific value on a molar basis		1,000 5	1,001 0	1,002 6	1,000 5	1,002 1	1,001 6
net calorific value on a molar basis		1,000 1	1,000 1	1,000 3	1,000 0	1,000 2	1,000 2
gross calorific value on a mass basis		1,000 5	1,001 0	1,002 6	1,000 5	1,002 1	1,001 6
net calorific value on a mass basis		1,000 1	1,000 1	1,000 3	1,000 0	1,000 2	1,000 2

Table 17 — Conversion factors for volume-basis calorific values and Wobbe indices

	combustion ($t_1/^\circ\text{C}$)/metering ($t_2/^\circ\text{C}$)											
	25/20 to 25/0	25/20 to 15/15	25/20 to 15/0	25/20 to 0/0	25/0 to 15/15	25/0 to 15/0	25/0 to 0/0	15/15 to 15/0	15/15 to 0/0	15/0 to 0/0	15/0 to 0/0	
a) volume basis ideal gross calorific value	1,073 2	1,018 4	1,074 3	1,076 0	0,948 9	1,001 0	1,002 6	1,054 9	1,056 6	1,001 6	1,001 6	
volume basis ideal net calorific value	1,073 2	1,017 5	1,073 3	1,073 5	0,948 1	1,000 1	1,000 3	1,054 9	1,055 1	1,000 2	1,000 2	
ideal gross Wobbe index	1,073 2	1,018 4	1,074 3	1,076 0	0,948 9	1,001 0	1,002 6	1,054 9	1,056 6	1,001 6	1,001 6	
ideal net Wobbe index	1,073 2	1,017 5	1,073 3	1,073 5	0,948 1	1,000 1	1,000 3	1,054 9	1,055 1	1,000 2	1,000 2	
volume basis real gross calorific value	1,073 8	1,018 5	1,074 9	1,076 6	0,948 5	1,001 0	1,002 6	1,055 3	1,057 0	1,001 6	1,001 6	
volume basis real net calorific value	1,073 8	1,017 6	1,073 9	1,074 1	0,947 7	1,000 1	1,000 3	1,055 3	1,055 5	1,000 2	1,000 2	
real gross Wobbe index	1,073 6	1,018 5	1,074 7	1,076 4	0,948 7	1,001 0	1,002 6	1,055 2	1,056 9	1,001 6	1,001 6	
real net Wobbe index	1,073 6	1,017 6	1,073 7	1,073 9	0,947 8	1,000 1	1,000 3	1,055 2	1,055 4	1,000 2	1,000 2	

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14.2 Equations for conversion between metric reference conditions

In ISO 13443:1996[75] equations are given that enable the conversion between reference states of the various physical properties that are the subject of both ISO 6976:2016 and this document.

These equations were originally intended specifically to provide a simple means by which to convert values of the properties from the various sets of reference conditions used throughout the world to corresponding values at ISO reference conditions ($T_1 = T_2 = 288,15$ K, $p_1 = p_2 = 101,325$ kPa, dry gas). It is self-evident, however, that they may be used in reverse to convert from ISO standard reference conditions to any other set of conditions within the ranges of applicability i.e. $270 < T/K < 300$ and $95 < p/\text{kPa} < 105$.

The equations are non-normative and are not exact. They use simple linear functions, for which values of the numerical constants (sensitivity coefficients) required are given in ISO 13443:1996[75], to approximate the complex variations with temperature of gross and net molar-basis calorific values $(Hc)_G^o$ and $(Hc)_N^o$ and of compression factor Z , from which all of the other properties follow by means that are fully detailed in ISO 13443.

The constants used in the equations have been determined by trial calculations for a wide range of natural gases. Despite this, it is important to note that the equations apply, like the conversion factors given in 14.1, only to mixtures that consist preponderantly of methane, with only minor amounts of higher hydrocarbon and inert components present, perhaps totalling no more than 10 % of the natural gas mixture. In general the equations may then be expected to achieve an accuracy within $\pm 0,05$ %. Nevertheless there is no specific guarantee of accuracy. Except for methane, the equations may not be used for pure components.

To use the equations, it is convenient first to calculate the target property of the mixture at ISO standard reference conditions and then convert the value to the required reference temperature (and, if relevant, pressure).

For the molar-basis calorific values, the relevant equations are

$$(Hc)_G(T_1) = (Hc)_G^o(T_1) = \frac{(Hc)_G^o(\text{ISO})}{[1 + 0,000\ 10 \times (T_1 - 288,15)]} \quad (81)$$

and

$$(Hc)_N(T_1) = (Hc)_N^o(T_1) = \frac{(Hc)_N^o(\text{ISO})}{[1 + 0,000\ 01 \times (T_1 - 288,15)]} \quad (82)$$

where (ISO) refers to the ISO standard reference conditions and $T_1 = t_1 + 273,15$ is the combustion reference temperature in kelvins.

For compression factor, the relevant equation is

$$Z(T_2, p_2) = Z(\text{ISO}) \times \frac{[1 + 0,000\ 025 \times (T_2 - 288,15)]}{[1 + 0,000\ 020 \times (p_2 - 101,325)]} \quad (83)$$

where $T_2 = t_2 + 273,15$ is the metering reference temperature and p_2 is the metering reference pressure.

For further and more detailed information, the user is referred directly to ISO 13443:1996[75].

14.3 Expression of non-SI reference (base) pressures in metric units

A number of non-SI combustion reference pressures p_1 and metering reference pressures p_2 (usually with $p_1 = p_2$) are, or have been, in use over the years, usually in conjunction with the reference

temperatures $t_1 = t_2 = 60\text{ }^\circ\text{F}$ respectively. The following prescriptions for these pressures may be identified:

- a) The standard atmosphere (metric standard pressure). The defined pressure is 101,325 kPa (1 013,25 mbar) exactly (derived historically from 760 mm of mercury at 0 °C subjected to standard gravity), which converts to approximately 14,695 95 psi, usually rounded to 14,696 psi. The rounded value is adopted in U.S. Gas Processors Association (GPA) documentation^[66].
- b) 30 in of mercury, where the mercury is at 60 °F and subjected to gravity as at latitude 53 degrees north (central England). The pressure so prescribed is equal to approximately 101,374 kPa. This is sometimes referred to as the Imperial standard pressure^{[76][77]}.

NOTE 1 This formulation was prescribed prior to metrication by the (then) Gas Standards Branch of the Department of Energy for use in official United Kingdom Gas Act testing.

- c) 30 in of mercury, where the mercury is at 32 °F (0 °C) and subjected to standard gravity (9,806 65 m·s⁻²). The pressure so prescribed is equal to approximately 101,592 kPa^{[76][78]}.

NOTE 2 This formulation was used prior to metrication by British Gas for contract purposes.

- d) U.S. customary pressure. Defined as 14,73 psi exactly (apparently derived historically from 762 mm of mercury), which converts to approximately 101,560 kPa^[7].
- e) 14,504 psi. This value, sometimes used in the U.S., is an approximate conversion (accurate to the third decimal place) from 100 kPa exactly, the latter adopted some time ago by IUPAC as a new standard pressure for use in chemical thermodynamics and thermochemistry^{[79][80]}.
- f) American Gas Association Report No 5 (AGA-5)^[81] lists a number of other base pressures used sometimes in the U.S., namely 14,4 psi, 14,65 psi and 15,025 psi (approximately equivalent to 99,285 kPa, 101,009 kPa and 103,594 kPa respectively), plus 98,066 5 kPa (equal to 1 kgf·cm⁻²), but their provenances are unclear.

Table 18 summarizes the equivalences of these various pressure bases.

Table 18 — SI equivalent values for non-SI base pressures

inches Hg	mm Hg	psi	kPa
			98,066 5
		14,4	99,285
		14,504	100,000
		14,65	101,009
	760 (at 0 °C)	14,696	101,325
30 (at 60 °F)			101,374
	762	14,73	101,560
30 (at 32 °F)			101,592
		15,025	103,594

15 Mathematical and methodological issues relating to estimation of uncertainty

15.1 Principles

In ISO 6976:2016 the uncertainty associated with any natural gas mixture property calculated from composition is evaluated and specified in accordance with the *Guide to the expression of uncertainty in measurement* (GUM)^[62].

NOTE GUM^[62] also provides definitions of those concepts (e.g. coverage factor) shown first in italic small-capital type when introduced in the next and subsequent paragraphs of 15.1 and 15.2.

The *UNCERTAINTY* of each such natural gas mixture property Y is expressed as an *EXPANDED UNCERTAINTY* $U(Y)$, given by the product $U(Y) = k \cdot u(Y)$ of a (*COMBINED*) *STANDARD UNCERTAINTY* $u(Y)$ and a *COVERAGE FACTOR* k . By default, the coverage factor is normally taken as $k = 2$, corresponding to a confidence level of approximately 95 %.

The (combined) standard uncertainty is calculated according to the procedures of uncertainty propagation presented in the GUM. To this end, the property Y under consideration is expressed as a function F such that

$$Y = F(y_1, y_2, y_3, \dots, y_n, q_1, q_2, q_3, \dots, q_m) \quad (84)$$

where y_1, y_2, \dots, y_n are those input quantities that have an associated uncertainty and q_1, q_2, \dots, q_m are those other parameters that are specified without uncertainty.

The function F can in principle be given by either a closed-form mathematical expression or a computer algorithm. [Formula \(84\)](#) may be specified either as a single equation or as a sequence of equations with specified substitution.

Given the “mathematical model” according to [Formula \(84\)](#), the (combined) standard uncertainty $u(Y)$ is calculated from

$$u^2(Y) = \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial F}{\partial y_i} \right) \cdot u(y_i) \cdot r(y_i, y_j) \cdot u(y_j) \cdot \left(\frac{\partial F}{\partial y_j} \right) \quad (85)$$

which expands to

$$u^2(Y) = \sum_{i=1}^N \left(\left(\frac{\partial F}{\partial y_i} \right)^2 \times u^2(y_i) \right) + \sum_{j=1}^N \sum_{\substack{k=1 \\ k \neq j}}^N \left(\left(\frac{\partial F}{\partial y_j} \right) \times u(y_j) \times r(y_j, y_k) \times u(y_k) \times \left(\frac{\partial F}{\partial y_k} \right) \right) \quad (86)$$

or

$$u^2(Y) = \sum_{i=1}^N \left(\left(\frac{\partial F}{\partial y_i} \right)^2 \times u^2(y_i) \right) + 2 \times \sum_{j=1}^{N-1} \sum_{k=j+1}^N \left(\left(\frac{\partial F}{\partial y_j} \right) \times u(y_j) \times r(y_j, y_k) \times u(y_k) \times \left(\frac{\partial F}{\partial y_k} \right) \right) \quad (87)$$

where

N is the number of input values of y ;

$u(y_i)$ is the standard uncertainty of input quantity y_i ;

$u^2(y_i)$ is the *VARIANCE* (squared standard uncertainty) of input quantity y_i ;

$r(y_i, y_j)$ is the *CORRELATION COEFFICIENT* between input quantities y_i and y_j ;

$\left(\frac{\partial F}{\partial y_i} \right)$ is the *SENSITIVITY COEFFICIENT* (partial derivative) of F (or Y) with respect to input quantity y_i ;

whence (taking the positive square root)

$$u(Y) = \sqrt{u^2(Y)} \quad (88)$$

For some purposes, correlations between input quantities may be ignored or neglected. In this case [Formula \(86\)](#) for the (combined) variance reduces to

$$u^2(Y) = \sum_{i=1}^N \left(\left(\frac{\partial F}{\partial y_i} \right)^2 \times u^2(y_i) \right) \quad (89)$$

Even [Formula \(89\)](#) is not in general amenable to easy evaluation, but it is clearly much more tractable than [Formula \(86\)](#) and, if there is good reason to exclude correlations, may be purposive.

[Formula \(86\)](#), however, remains the full and proper mathematical expression for the complete uncertainty budget for any property Y , and a methodology for its practical numerical evaluation for each of the properties calculated by the methods described in ISO 6976:2016 is the subject of the remainder of [Clause 15](#).

Unfortunately the estimation of the relevant correlation coefficients, so as to be able to include all terms on the right-hand side of [Formula \(86\)](#), is never an easy task and, for lack of sufficiently detailed information about how the input data were determined, may sometimes be amenable only to approximation or, indeed, impossible.

15.2 Input data

15.2.1 Preamble

For natural gas mixture properties Y calculated from molar composition, the mathematical model given as [Formula \(84\)](#) reduces to the sequence of equations specified in ISO 6976:2016, Clauses 7 to 10. These equations use three distinct kinds of input data, namely

- a) reference conditions
- b) composition data
- c) physical property data.

Each of these is now considered in turn.

15.2.2 Reference conditions

The reference conditions of pressure and temperature to which the calculations in ISO 6976:2016 apply appear explicitly in the equations for calculation of some of the properties. In the context of [Formula \(84\)](#) they are parameters specified without uncertainty i.e. they are specified exactly.

15.2.3 Composition data

The composition data required as input data for ISO 6976:2016 is a complete set of mole fractions and their associated uncertainties.

Complete analyses of composition by gas chromatography inevitably and unavoidably involve implicit correlations between each mole fraction and each other mole fraction^[82]. This remains true whether the composition of a natural gas is determined on the basis of the measurement of each and every

component (in short “methane by analysis”) or on the basis of the measurement of every component except methane (“methane by difference”).

NOTE In the case of methane by analysis it is usual that the raw experimental amount fraction data (pseudo mole fractions) x_i^* are forced to sum to unity by *normalization* i.e. by applying the operation $x_i = x_i^*/\sum x_i^*$ for all components. This process introduces correlation, but it is *not* the case that the pre-normalized values can be considered as uncorrelated.

Attempts to take into account these correlations lead to treatments which, at the level of mathematical skills that can reasonably be expected of typical ‘everyday’ users of ISO 6976:2016, are less than straightforward to handle. However, a variety of users, for example those working in technically advanced industrial laboratories, or those working for accreditation bodies, will need wherever possible to take these correlations into account in the estimation of a complete uncertainty budget.

For reasons, therefore, of practicality, it is often convenient and sufficient to assume that the input provided for ISO 6976:2016 by gas-chromatographic analytical methods, as described, for example, in ISO 6974-1:2012[83] and ISO 6974-2:2012[84], consists of a complete analysis by mole fraction, including uncertainties, in which the separate values of mole fraction may falsely be taken as uncorrelated. It may be shown[82] that the exclusion of correlations nearly always leads to an over-estimate of uncertainty in the calculated value of a physical property for a typical natural gas. For an explanation of this, see 16.3.1. In the present context, an over-estimate is clearly preferable to an under-estimate.

It is often further assumed that the uncertainty associated with each mole fraction is uncorrelated with the uncertainty of each other mole fraction, although this too is not strictly valid[85].

Returning to [Formula \(86\)](#), the set of correlation coefficients $r(x_i, x_j)$ may be expressed in the form of a matrix, known as a *CORRELATION COEFFICIENT MATRIX*[62] (or, not quite correctly, as a *VARIANCE-COVARIANCE MATRIX*). The assumption that the analytical composition values are uncorrelated is equivalent to setting the on-diagonal elements ($i = j$) to unity and the off-diagonal elements ($i \neq j$) to zero (this form is known as an *identity matrix*). However if the analytical data can be evaluated in such a way as to provide a non-zero set of off-diagonal correlation coefficients, then these can, and should, be incorporated into the matrix.

15.2.4 Physical property data

The physical property data required as input for ISO 6976:2016 are as follows:

a) Component data

For each of the sixty molecular species listed in ISO 6976:2016 as possible components of a natural gas or similar mixture, values of the following properties, including (in principle) associated uncertainties, are required:

- standard enthalpy of combustion H_c^o at 25 °C, 20 °C, 60 °F, 15 °C, 0 °C;
- summation factor s at 20 °C, 60 °F, 15 °C, 0 °C;
- molar mass M .

In reality, uncertainties for those components that are never present in natural gas or similar mixtures at mole fractions of greater than about 0,01 may, in terms of their impact on the overall uncertainty, safely be ignored. This reduces the set of molecular species for which the uncertainty is required from 60 to 12, namely methane, ethane, propane, n-butane, 2-methylpropane, n-pentane, 2-methylbutane, 2,2-dimethylpropane, nitrogen, carbon dioxide, hydrogen and carbon monoxide. For the sake of rigour and completeness, however, the tabulations in ISO 6976:2016 include uncertainty estimates for all properties of all components.

b) Auxiliary data

The required auxiliary data (including uncertainties) comprise

- standard enthalpy of vaporization of water at 25 °C, 20 °C, 60 °F, 15 °C, 0 °C, and

- compression factor of dry air at 20 °C, 60 °F, 15 °C, 0 °C.

The values of the molar gas constant R and the molar mass of air M_{air} may also be counted among the auxiliary data, but both have standard uncertainties of less than 10^{-5} relative which, for most applications, may perhaps be considered as negligibly small (but, again, for rigour and completeness, are not excluded).

15.3 Uncertainty of the calculational method

When the model [Formula \(84\)](#) is not exact i.e. when it is based on an approximation, and when the uncertainty associated with this approximation is likely to contribute significantly to the combined standard uncertainty, then the model equation has to be amended to account for the approximation error. Simple procedures for this purpose are

- adding a correction term $\zeta = 0$ with $u(\zeta) > 0$, and
- multiplying by a correction factor $\eta = 1$ with $u(\eta) > 0$.

In the present context there are two sources of potential uncertainty of the calculational method.

Firstly, the assumption that, for all natural gases, the residual enthalpy of combustion [$H_c - H_c^o$] (enthalpic correction) is negligible, may be identified as an approximation. This approximation is mentioned (and dismissed without further consideration) in ISO 6976:2016, Clause 5. The justification for ignoring the effect of this approximation is discussed fully in [Clause 6](#), where it is estimated that a typical value of the enthalpic correction is roughly 0,01 kJ·mol⁻¹, or about 0,001 % of the enthalpy of combustion.

Although the neglect of this factor introduces a bias (rather than a random error) into the method, this may safely be ignored by comparison with other sources of uncertainty. To place the enthalpic correction in perspective, its value is about one twentieth of the measurement uncertainty in the enthalpy of combustion of methane.

A more significant source of uncertainty in the calculational method may come from ISO 6976:2016, Formula (3) [[Formula \(34\)](#)] for the compression factor of a natural gas mixture. The reasons why this is so are addressed in [7.4](#) and will not be repeated here. Suffice to say that as the number of non-methane components in the natural gas mixture increases, and as the amount of each such component also increases, the uncertainty in compression factor likewise also increases.

This issue may be addressed by the inclusion in [Formula \(34\)](#), as indicated above, of either a correction term $\zeta = 0$ or a correction factor $\eta = 1$ for which $u(\zeta) > 0$ or $u(\eta) > 0$ respectively. The problem then becomes that of how to estimate $u(\zeta)$ or $u(\eta)$.

However, as discussed more fully in [7.5](#) and [8.5](#), the necessity to adopt either of these strategies has been avoided by the inclusion of extra uncertainties in the values of summation factor $s_i(t_2, p_0)$ that are tabulated in ISO 6976:2016.

15.4 Evaluation of sensitivity coefficients

15.4.1 Preamble

In order to obtain values for the many sensitivity coefficients $\partial F/\partial y_i$ required for use in [Formula \(86\)](#) or [\(87\)](#), for each of the calculated properties Y , at least three viable methods are available, namely

- a) an analytical method,
- b) a finite difference method, and
- c) a Monte Carlo simulation method.

Each of these is now considered in turn.

15.4.2 Analytical method

In the context of ISO 6976:2016, the function F for which it is required to estimate the uncertainty is always a physical property (such as a calorific value) that is given by a closed-form mathematical expression. In consequence the sensitivity coefficients $\partial F/\partial y_i$ may always be determined analytically as partial derivatives.

Equations resulting from the application of this method are given for each property in ISO 6976:2016, Annex B. The detailed transformations required to get from [Formula \(86\)](#) to the equations given in ISO 6976:2016, Annex B are presented in [Clause 16](#). Use of these equations is the normative method for the calculation of uncertainty.

The expressions given in ISO 6976:2016, Annex B may appear somewhat formidable and (to some) perhaps out of proportion to the task at hand, but their implementation as part of a computer programme is in fact reasonably straightforward.

Notice that no sensitivity coefficients appear explicitly as partial derivatives in any of the equations for $u(Y)$ given in ISO 6976:2016, Annex B. As it turns out these may all be written completely in terms of the composition (including uncertainties) of the mixture and of the physical properties (including uncertainties) of the components of the mixture.

Notice also the correlation coefficients that appear in the equations for uncertainty. As expected, the elements $r(x_i, x_j)$ of the correlation matrix for mole fractions appear in every equation in ISO 6976:2016, Annex B but, in addition, the elements $r(M_i, M_j)$ of the correlation matrix for molar masses also appear in some of the equations. The off-diagonal elements of this matrix are mostly non-zero because each value of M_i uses the same values of atomic weight in its determination. The normative method for calculating the required values of $r(M_i, M_j)$ is given as [Formula \(108\)](#) and reproduced as ISO 6976:2016, Formula (24). The derivation of this equation is detailed in [16.3.2](#).

NOTE [Table 19](#) lists values of the correlation coefficients $r(M_i, M_j)$ for the 11 most common constituents of a typical natural gas, calculated in accordance with [Formula \(108\)](#). The table is non-normative and is for convenience only.

Finally, it should be noted that, although no further correlation coefficients appear explicitly in the equations given in ISO 6976:2016, Annex B, it has been necessary to take into account the implicit correlation between, for example, molar calorific value and molar mass in the derivation of the uncertainty equation for mass-basis calorific value, and between molar calorific value and compression factor in the derivation for volume-basis calorific value. In each case (and in others) the two input properties are, of course, highly correlated by virtue of sharing the same input composition (see also [16.3.3](#)).

Table 19 — Correlation coefficients $r(M_i, M_j)$ for the molar masses of major components of natural gas

	$i = \text{CH}_4$	C_2H_6	C_3H_8	$\text{n-C}_4\text{H}_{10}$	$\text{iso-C}_4\text{H}_{10}$	$\text{n-C}_5\text{H}_{12}$	$\text{iso-C}_5\text{H}_{12}$	$\text{neo-C}_5\text{H}_{12}$	$\text{n-C}_6\text{H}_{14}$	N_2	CO_2
$j = \text{CH}_4$	1,000 000	0,996 804	0,994 234	0,992 650	0,992 650	0,991 603	0,991 603	0,991 603	0,990 864	0,000 000	0,755 087
C_2H_6	0,996 804	1,000 000	0,999 622	0,999 145	0,999 145	0,998 764	0,998 764	0,998 764	0,998 471	0,000 000	0,773 785
C_3H_8	0,994 234	0,999 623	1,000 000	0,999 903	0,999 903	0,999 753	0,999 753	0,999 753	0,999 613	0,000 000	0,779 073
$\text{n-C}_4\text{H}_{10}$	0,992 650	0,999 145	0,999 903	1,000 000	1,000 000	0,999 965	0,999 965	0,999 965	0,999 903	0,000 000	0,781 520
$\text{iso-C}_4\text{H}_{10}$	0,992 650	0,999 145	0,999 903	1,000 000	1,000 000	0,999 965	0,999 965	0,999 965	0,999 903	0,000 000	0,781 520
$\text{n-C}_5\text{H}_{12}$	0,991 603	0,998 764	0,999 753	0,999 965	0,999 965	1,000 000	1,000 000	1,000 000	0,999 985	0,000 000	0,782 923
$\text{iso-C}_5\text{H}_{12}$	0,991 603	0,998 764	0,999 753	0,999 965	0,999 965	1,000 000	1,000 000	1,000 000	0,999 985	0,000 000	0,782 923
$\text{neo-C}_5\text{H}_{12}$	0,991 603	0,998 764	0,999 753	0,999 965	0,999 965	1,000 000	1,000 000	1,000 000	0,999 985	0,000 000	0,782 923
$\text{n-C}_6\text{H}_{14}$	0,990 864	0,998 471	0,999 613	0,999 903	0,999 903	0,999 985	0,999 985	0,999 985	1,000 000	0,000 000	0,783 830
N_2	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000	0,000 000
CO_2	0,755 087	0,773 785	0,779 073	0,781 520	0,781 520	0,782 923	0,782 923	0,782 923	0,783 830	0,000 000	1,000 000

NOTE The values shown in this table have been calculated using ISO 6976:2016, Formula (24) [Formula (108)] with values of $u(A) = 0,000 4$ for C, 0,000 035 for H, 0,000 1 for N and 0,000 15 for O, as given in ISO 6976:2016, A.2 (half-values of $U(A)$ given in Table 6), and rounding to six places of decimal. It is emphasized that this table is only for guidance to the user in verifying their own implementation of the relevant equations, and is non-normative.

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15.4.3 Finite difference method

Sensitivity coefficients $\partial F/\partial y_i$ for use in [Formula \(86\)](#) may also be estimated by use of a finite difference method. The general equation for this procedure is

$$\frac{\partial F}{\partial y_i} \approx \frac{F\left(y_i + \frac{u(y_i)}{2}\right) - F\left(y_i - \frac{u(y_i)}{2}\right)}{u(y_i)} \quad (90)$$

This method is not very useful in respect of ISO 6976:2016, and so is not considered further here.

15.4.4 Monte Carlo method

The Monte Carlo simulation method is a computer-driven technique that can provide a perfectly acceptable alternative to either the analytical or finite difference methods for the estimation of either individual sensitivity coefficients or, more usually and more usefully, of complete uncertainty. Some purists might consider the method as the 'brute force' application of computer power, but nevertheless it is internationally recognized as an accurate and viable method. The principles and methodology of the Monte Carlo method have been formally published by ISO and other authoritative bodies^[86].

The Monte Carlo methodology has been implemented in a number of commercially available computer packages, including the GasTools[®] Excel[®] add-in to GasVLe^{®3)}.

In essence the method is simple. The user is required to provide all of the input data that are needed for the calculation of a chosen property in accordance with a chosen algorithm. For each of the input quantities the user is also required to provide a probability density (distribution) function (e.g. Gaussian) and a measure (e.g. standard deviation) that together provide a mathematical description of the uncertainty associated with the input quantity.

When each of these quantities has been properly defined, the Monte Carlo computer package is set so as to perform a large number (maybe 100,000) of calculations of the target property using the relevant algorithm. For each individual calculation each input parameter is simultaneously selected as a probability-weighted random value from within its own probability density function. More detail about general procedures in Monte Carlo simulation is given elsewhere^[86].

The result of this operation is a large set of output property data, the individual values of which are scattered about a mean value in accordance with an overall pattern of distribution that is an accurate reflection of the various input uncertainties.

The mean value may be interpreted as the 'best estimate' value of the property determined and the pattern of distribution may be interpreted as a measure, usually expressed as a standard deviation, of the overall standard uncertainty of calculation.

The Monte Carlo method is properly applicable to the calculation of uncertainty for the purposes of ISO 6976:2016, but is not the normative method.

16 Detailed derivation of uncertainty equations in ISO 6976:2016

16.1 Principles and assumptions

The purpose of this clause is to derive the equations given in ISO 6976:2016, Annex B for the estimation of the uncertainties in the thermophysical properties to which the standard is applied. The over-riding principle is that these uncertainties are to be calculated in accordance with the rules enumerated in the *Guide to the expression of uncertainty in measurement* (GUM)^[62]. Some general introductory material in this respect has been given in [Clause 15](#).

3) GasVLe[®] is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

The following specific assumptions are made in respect of the input data (symbols are listed fully in [Clause 4](#)):

- a) that values of the constant quantities R (molar gas constant) and M_{air} (molar mass of air) are available (as provided in the standard),
- b) that values of the temperature dependent quantities Z_{air} (compression factor of air) and L^o (standard enthalpy of vaporization of water) are available at each of the relevant reference temperatures (as provided in the standard),
- c) that values of the constant quantities M_i (molar mass) and b_i (hydrogen-atom index) are available for each of the sixty components considered in ISO 6976:2016 (as provided in the standard),
- d) that values of the temperature dependent quantities s_i (summation factor) and $[(Hc)_G^o]_i$ (standard enthalpy of combustion) are available for each of the sixty components at each of the relevant reference temperatures (as provided in the standard),
- e) that values of the standard uncertainties $u(R)$, $u(M_{\text{air}})$, $u(Z_{\text{air}})$, $u(L^o)$, $u(M_i)$, $u(s_i)$ and $u([(Hc)_G^o]_i)$ that correspond to each of the quantities listed in a) to d) (except for b_i , which has zero uncertainty) are available (as provided in the standard or, in the case of $u(M_i)$, made available by specified calculation from values of uncertainty in atomic mass $u(A)$ for C, H, N, O, S, etc. provided in the standard),
- f) that a complete set of component mole fractions x_i is available (to be provided by the user),
- g) that a corresponding complete set of component mole fraction uncertainties $u(x_i)$ is available (to be provided by the user),
- h) that a set (matrix) of correlation coefficients $r(x_i, x_j)$ for the component mole fractions is either available (provided by the user) or, in the absence of better information, assumed to be the elements of an identity matrix (see [15.2.3](#)),
- i) that there are no correlations (covariance) between any physical property Y_i of component i (as given in a) to d)) and the same physical property Y_j of any other component j (except for molar masses M_i , for which, see [16.3.2](#)),
- j) that there are no correlations (covariance) between any physical property $(Y_A)_i$ of component i (as given in a) to d)) and any other physical quantity $(Y_B)_i$ of the same component at the same temperature, and
- k) that there are no correlations (covariance) between any of the physical properties Y_i and any of the component mole fractions x_i .

16.2 General formulation

The general expression for the calculation of the physical property Y from a complete composition plus the relevant component physical properties and other input is given as [Formula \(84\)](#), repeated here –

$$Y = F(y_1, y_2, y_3, \dots, y_n, q_1, q_2, q_3, \dots, q_m) \quad (91)$$

where

y_1, y_2, \dots, y_n are those input quantities that have an associated uncertainty;

q_1, q_2, \dots, q_m are those other parameters that are specified without uncertainty.

In accordance with GUM[62] the variance (squared standard uncertainty) may be written as [Formula \(85\)](#), also repeated here -

$$u^2(Y) = \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial F}{\partial y_i} \right) \cdot u(y_i) \cdot r(y_i, y_j) \cdot u(y_j) \cdot \left(\frac{\partial F}{\partial y_j} \right) \quad (92)$$

For the particular case where the property is 'basic' in the sense of being formed as the mole fraction average of component properties, [Formula \(91\)](#) reduces to

$$Y = \sum_{i=1}^N x_i \cdot Y_i \quad (93)$$

And, if assumptions [16.1 j\)](#) and [16.1 k\)](#) are valid, [Formula \(92\)](#) reduces to

$$u^2(Y) = \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial Y}{\partial x_i} \right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) \cdot \left(\frac{\partial Y}{\partial x_j} \right) + \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial Y}{\partial Y_i} \right) \cdot u(Y_i) \cdot r(Y_i, Y_j) \cdot u(Y_j) \cdot \left(\frac{\partial Y}{\partial Y_j} \right) \quad (94)$$

where the elements $r(x_i, x_j)$ of the mole fraction correlation coefficient matrix are given by

$$r(x_i, x_j) = u(x_i, x_j) / u(x_i) \cdot u(x_j) \quad (95)$$

and where $u(x_i, x_j)$ is the covariance between x_i and x_j (with an analogous relation applicable to $r(Y_i, Y_j)$). By partial differentiation of [Formula \(93\)](#), the sensitivity coefficients in [Formula \(94\)](#) may be replaced so as to give

$$u^2(Y) = \left(\sum_{i=1}^N \sum_{j=1}^N Y_i \cdot Y_j \cdot u(x_i) \cdot u(x_j) \cdot r(x_i, x_j) \right) + \left(\sum_{i=1}^N \sum_{j=1}^N x_i \cdot x_j \cdot u(Y_i) \cdot u(Y_j) \cdot r(Y_i, Y_j) \right) \quad (96)$$

which may also be written as

$$u^2(Y) = \left(\sum_{i=1}^N Y_i \cdot u(x_i) \times \sum_{j=1}^N r(x_i, x_j) \cdot Y_j \cdot u(x_j) \right) + \left(\sum_{i=1}^N x_i \cdot u(Y_i) \times \sum_{j=1}^N r(Y_i, Y_j) \cdot x_j \cdot u(Y_j) \right) \quad (97)$$

If Y_i and Y_j are uncorrelated [assumption [16.1 i\)](#)] then the off-diagonal elements of the correlation matrix $r(Y_i, Y_j)$ are all zero, and [Formula \(97\)](#) becomes

$$u^2(Y) = \left(\sum_{i=1}^N Y_i \cdot u(x_i) \times \sum_{j=1}^N r(x_i, x_j) \cdot Y_j \cdot u(x_j) \right) + \sum_{i=1}^N x_i^2 \cdot u^2(Y_i) \quad (98)$$

16.3 Effects of correlations

16.3.1 Correlation between mole fractions

The inevitable and unavoidable strong correlations among mole fractions determined by gas chromatography are discussed at some length in [15.2.3](#), and that discussion need not be repeated or elaborated further here.

In practice it is unlikely that the elements $r(x_i, x_j)$ of the correlation coefficient matrix for the mole fractions will often be available for use in the equations given in ISO 6976:2016, Annex B, which are all derived as shown below in [16.4](#) and [16.5](#) from [Formula \(92\)](#). In this situation the advice given in

ISO 6976:2016 is to replace the true (unknown) correlation coefficient matrix by an identity matrix, that is a matrix for which the on-diagonal ($i = j$) elements are unity and the off-diagonal ($i \neq j$) elements are zero. The claim, based in part on the work of Hässelbarth and Bremser^[82], is that this approximation (almost) always leads to a (safe) over-estimate of uncertainty for the property in question. The purpose of this subclause is to explain and expand the justification for that claim.

The constraint that the sum S of all mole fractions is unity may be written as

$$S = \sum_{i=1}^N x_i \tag{99}$$

where $S = 1$ and $u(S) = 0$.

Application of [Formula \(92\)](#) to [Formula \(99\)](#) leads directly to

$$u^2(S) = \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial S}{\partial x_i} \right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) \cdot \left(\frac{\partial S}{\partial x_j} \right) \tag{100}$$

whence

$$u^2(S) = \sum_{i=1}^N \sum_{j=1}^N u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) \tag{101}$$

since [from [Formula \(99\)](#)] all $\left(\frac{\partial S}{\partial x_i} \right) = 1$.

Furthermore, since $u^2(S) = 0$, [Formula \(101\)](#) may be rewritten as

$$\sum_{i=1}^N u^2(x_i) + 2 \times \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) = 0 \tag{102}$$

Now, since $u^2(x_i) > 0$ the second summation of [Formula \(102\)](#) is necessarily negative. Since also $u(x_i)$ and $u(x_j) > 0$, it follows that there are necessarily a sufficient number of negative off-diagonal correlation coefficients to ensure that the zero-sum of the equation is satisfied.

It is easy to see, for example from [Formula \(94\)](#), that any negative off-diagonal element of a correlation matrix reduces the uncertainty below the result obtained by taking it as zero. Hence there is a tendency for the total uncertainty to be over-estimated by taking all off-diagonal elements as zero.

This indeed is the general observation that has been made in practice, and which seems to be predominantly valid. It should be recognized, however, that this is not in principle a hard-and-fast rule. The reason is that not all off-diagonal correlation coefficients need necessarily be negative for [Formula \(102\)](#) to be satisfied, and the effect upon [Formula \(94\)](#) of each term, positive or negative, depends also upon the magnitude and sign of the associated sensitivity coefficients.

16.3.2 Correlation between molar masses

If any two component molecular species of a mixture include at least one atomic species in common, then the molar masses (molecular weights) of the two molecular species are correlated (covariant). For example, the molar masses of methane and carbon dioxide are correlated by virtue of both containing atoms of carbon, the molar masses of methane and ethane are highly correlated by virtue of both containing atoms of carbon and of hydrogen, whereas the molar masses of methane and nitrogen are uncorrelated because they share no atomic species in common. The uncertainties in the molar masses are likewise (correspondingly) correlated or uncorrelated in these respective examples.

It is important to take correlations of this kind into account in evaluating the uncertainty of several of the physical quantities considered in ISO 6976:2016. The equations given in [16.4](#) and [16.5](#) and in ISO 6976:2016, Annex B include these correlations where appropriate. The equation to be used for

calculating the required correlation coefficients is given as ISO 6976:2016, Formula (24). The purpose of this subclause is to justify the derivation of that equation.

For the component i having the molecular formula $(C_aH_bN_cO_dS_e)_i$ the molar mass M_i is given by

$$M_i = a_i \cdot A_C + b_i \cdot A_H + c_i \cdot A_N + d_i \cdot A_O + e_i \cdot A_S \quad (103)$$

where A_C is the atomic weight of carbon, and so on.

The uncertainty in M_i is then given by

$$u^2(M_i) = a_i^2 \cdot u^2(A_C) + b_i^2 \cdot u^2(A_H) + c_i^2 \cdot u^2(A_N) + d_i^2 \cdot u^2(A_O) + e_i^2 \cdot u^2(A_S) \quad (104)$$

The covariance between M_i and the molar mass M_j of a second molecular species j is given by

$$u(M_i, M_j) = \left(\frac{\partial M_i}{\partial A_C} \right) \cdot \left(\frac{\partial M_j}{\partial A_C} \right) \cdot u^2(A_C) + \left(\frac{\partial M_i}{\partial A_H} \right) \cdot \left(\frac{\partial M_j}{\partial A_H} \right) \cdot u^2(A_H) + \left(\frac{\partial M_i}{\partial A_N} \right) \cdot \left(\frac{\partial M_j}{\partial A_N} \right) \cdot u^2(A_N) \\ + \left(\frac{\partial M_i}{\partial A_O} \right) \cdot \left(\frac{\partial M_j}{\partial A_O} \right) \cdot u^2(A_O) + \left(\frac{\partial M_i}{\partial A_S} \right) \cdot \left(\frac{\partial M_j}{\partial A_S} \right) \cdot u^2(A_S) \quad (105)$$

By straightforward partial differentiation this reduces to

$$u(M_i, M_j) = a_i \cdot a_j \cdot u^2(A_C) + b_i \cdot b_j \cdot u^2(A_H) + c_i \cdot c_j \cdot u^2(A_N) + \\ d_i \cdot d_j \cdot u^2(A_O) + e_i \cdot e_j \cdot u^2(A_S) \quad (106)$$

The correlation coefficients are then defined by

$$r(M_i, M_j) = u(M_i, M_j) / u(M_i) \cdot u(M_j) \quad (107)$$

from which

$$r(M_i, M_j) = \left(\frac{a_i \cdot a_j \cdot u^2(A_C) + b_i \cdot b_j \cdot u^2(A_H) + c_i \cdot c_j \cdot u^2(A_N) + d_i \cdot d_j \cdot u^2(A_O) + e_i \cdot e_j \cdot u^2(A_S)}{u(M_i) \cdot u(M_j)} \right) \quad (108)$$

which, in general, is clearly non-zero and, for $i = j$, is equal to unity. This equation is given as ISO 6976:2016, Formula (24).

Table 19 lists values of the correlation coefficients $r(M_i, M_j)$ derived using this equation for the eleven most common constituents of a typical natural gas. Notice that for molar masses, unlike the case for mole fractions, those correlation coefficients $r(M_i, M_j)$ that are neither zero nor unity are all positive. This implies that the effect of properly taking these correlations into account is always to increase the uncertainty in the molar mass of the gas mixture (see [16.4.1](#)) and, by further implication, to increase the uncertainty of any other property that uses molar mass in its calculation – or, more precisely, the effect of not accounting for these correlations is to underestimate the uncertainty.

In order to comply normatively with ISO 6976:2016 the user is required always to use [Formula \(108\)](#) above or ISO 6976:2016, Formula (24), not [Table 19](#), to determine values of $r(M_i, M_j)$. The table is, of course, only a partial representation of the full 60×60 -component matrix.

NOTE In principle there is also a minor correlation between the molar mass M_{air} of air and the molar mass M of any mixture that contains any of the components of air, but this is ignored in the equations developed in [16.5](#) for uncertainty in relative density and Wobbe indices.

16.3.3 Correlation between physical properties

Although it may be safe to assert, as required by assumption [16.1 j\)](#), that no correlation exists between the three fundamental input properties M_i , $[(Hc)_G^o]_i$ and s_i for any component i , it is not correct to assume that no correlation exists between the same properties M , $(Hc)_G^o$ and s for a natural gas mixture. These properties are indeed strongly correlated by virtue of sharing the same set of input mole fractions. Consequently any other mixture property that is formed as a combination of these properties has implicit correlations that need to be accounted for when deriving equations to express the uncertainty of such a compound property.

For example, for the mass-basis gross calorific value, calculated as

$$(Hm)_G = (Hc)_G / M \tag{109}$$

it does not follow that the relative uncertainties in $(Hc)_G$ and M can be combined as usual in quadrature to give the relative uncertainty in $(Hm)_G$, that is

$$u^2 \left(\frac{(Hm)_G}{(Hm)_G} \right) \neq u^2 \left(\frac{(Hc)_G}{(Hc)_G} \right) + u^2 \left(\frac{M}{M} \right) \tag{110}$$

because $(Hc)_G$ and M are significantly correlated.

Other examples of properties for which correlations of this sort need to be taken into account are volume-basis calorific values ($(Hc)_G$ and s), density and relative density (M and s) and Wobbe indices ($(Hc)_G$, M and s). Uncertainty equations for these compound properties are derived in [16.5](#).

16.4 Uncertainty equations for basic properties

16.4.1 Molar mass

For the calculation of the mean molar mass M of a mixture, [Formula \(93\)](#) becomes

$$M = \sum_{i=1}^N x_i \cdot M_i \tag{111}$$

and the uncertainty $u(M)$ of this quantity is obtained by replacing Y in [Formula \(96\)](#) by M as follows

$$u^2(M) = \left(\sum_{i=1}^N \sum_{j=1}^N M_i \cdot M_j \cdot u(x_i) \cdot u(x_j) \cdot r(x_i, x_j) \right) + \left(\sum_{i=1}^N \sum_{j=1}^N x_i \cdot x_j \cdot u(M_i) \cdot u(M_j) \cdot r(M_i, M_j) \right) \tag{112}$$

This equation cannot be simplified further because, in general, the off-diagonal elements $r(M_i, M_j)$ of the correlation matrix are not zero. For details of how to evaluate the elements of $r(M_i, M_j)$ see [16.3.2](#). This equation is given in ISO 6976:2016, Formula (B.1).

16.4.2 Molar-basis gross calorific value

For the calculation of the molar-basis gross calorific value $(Hc)_G^o$ of a mixture, [Formula \(93\)](#) becomes

$$(Hc)_G^o = \sum_{i=1}^N x_i \cdot [(Hc)_G^o]_i \quad (113)$$

In this case, it is reasonable (though not unchallengeable) to assume that values of $[(Hc)_G^o]_i$ are uncorrelated. For the purposes of ISO 6976:2016 it is further assumed throughout (and justified in [6.3](#)) that the real-gas value $(Hc)_G$ of the molar-basis gross calorific value is essentially identical with the ideal-gas value $(Hc)_G^o$. Consequently the uncertainty $u(Hc)_G$ of this quantity is obtained by replacing Y in [Formula \(98\)](#) by $(Hc)_G^o$ and rewriting in slightly different form as follows

$$u^2(Hc)_G = \left(\sum_{i=1}^N \sum_{j=1}^N \left[[(Hc)_G^o]_i \cdot u(x_i) \cdot r(x_i, x_j) \cdot [(Hc)_G^o]_j \cdot u(x_j) \right] + \sum_{i=1}^N x_i^2 \cdot u^2 \left(\left[[(Hc)_G^o]_i \right] \right) \right) \quad (114)$$

This equation is given as ISO 6976:2016, Formula (B.4).

16.4.3 Molar-basis net calorific value

In this case, [Formula \(93\)](#) becomes

$$(Hc)_N^o = \sum_{i=1}^N x_i \times \left(\left[[(Hc)_G^o]_i \right] - \frac{L^o}{2} \cdot b_i \right) \quad (115)$$

where L^o is the standard enthalpy of vaporization of water and b_i is the atomic index for hydrogen (the latter known exactly and without uncertainty) of component i .

Since $[(Hc)_G^o]_i$, L^o and b_i are all uncorrelated, the uncertainty $u(Hc)_N$ may be written as the analogue of [Formula \(114\)](#), as follows:

$$u^2(Hc)_N = \left(\sum_{i=1}^N \sum_{j=1}^N \left(\left[[(Hc)_G^o]_i \right] - \frac{L^o}{2} \cdot b_i \right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot \left(\left[[(Hc)_G^o]_j \right] - \frac{L^o}{2} \cdot b_j \right) \cdot u(x_j) \right) + \sum_{i=1}^N x_i^2 \cdot u^2 \left(\left[[(Hc)_G^o]_i \right] - \frac{L^o}{2} \cdot b_i \right) \quad (116)$$

And by separating out and combining in quadrature the independent uncertainties from $[(Hc)_G^o]_i$ and L^o in the last summation, this becomes

$$u^2(Hc)_N = \left(\sum_{i=1}^N \sum_{j=1}^N \left(\left[(Hc)_G^o \right]_i - \frac{L^o}{2} \cdot b_i \right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot \left(\left[(Hc)_G^o \right]_j - \frac{L^o}{2} \cdot b_j \right) \cdot u(x_j) \right) + \sum_{i=1}^N x_i^2 \cdot u^2 \left(\left[(Hc)_G^o \right]_i \right) + \sum_{i=1}^N \left(\frac{x_i \cdot b_i}{2} \right)^2 \cdot u^2(L^o) \quad (117)$$

This equation is given as ISO 6976:2016, Formula (B.8).

Given that $(Hc)_G^o$ and $(Hc)_G$ are taken as identically equal, the superscript (o) on this quantity is not strictly necessary in [Formulae \(114\)](#) and [\(117\)](#) and, for convenience and clarity, is therefore omitted from subsequent equations.

16.4.4 Summation factor

For the calculation of the summation factor s of a mixture, [Formula \(93\)](#) becomes

$$s = \sum_{i=1}^N x_i \cdot s_i \quad (118)$$

As was the case for molar-basis gross calorific value $[(Hc)_G^o]_i$, it is reasonable to assume that values s_i of are uncorrelated. The uncertainty $u(s)$ may therefore be obtained from the exact analogue of [Formula \(114\)](#), as follows:

$$u^2(s) = \left(\sum_{i=1}^N \sum_{j=1}^N s_i \cdot u(x_i) \cdot r(x_i, x_j) \cdot s_j \cdot u(x_j) \right) + \sum_{i=1}^N x_i^2 \cdot u^2(s_i) \quad (119)$$

This equation is given as ISO 6976:2016, Formula (B.2).

16.4.5 Compression factor

By definition, the compression factor Z of a mixture is related to the summation factor s at the same temperature and pressure by the equation

$$Z = 1 - s^2 \quad (120)$$

whence

$$u(Z) = 2 \cdot s \cdot u(s) \quad (121)$$

Consequently, by combination of [Formulae \(119\)](#) and [\(121\)](#), the standard uncertainty of Z may be obtained from

$$u^2(Z) = 4 \cdot s^2 \times \left(\left(\sum_{i=1}^N \sum_{j=1}^N s_i \cdot u(x_i) \cdot r(x_i, x_j) \cdot s_j \cdot u(x_j) \right) + \sum_{i=1}^N x_i^2 \cdot u^2(s_i) \right) \quad (122)$$

This equation is given as ISO 6976:2016, Formula (B.3).

16.5 Uncertainty equations for compound properties

16.5.1 Mass-basis gross calorific value

The defining equation for mass-basis gross calorific value $(Hm)_G$ is

$$(Hm)_G = (Hc)_G / M \quad (123)$$

or, in terms of the basic input variables x_i , M_i and $[(Hc)_G]_i$

$$(Hm)_G = \frac{\sum_{i=1}^N x_i \cdot [(Hc)_G]_i}{\sum_{i=1}^N x_i \cdot M_i} \quad (124)$$

The sensitivity coefficients to each of the three basic input variables may be readily obtained by partial differentiation, as follows

$$\left(\frac{\partial (Hm)_G}{\partial x_i} \right) = (Hm)_G \cdot \left(\frac{[(Hc)_G]_i}{(Hc)_G} - \frac{M_i}{M} \right) \quad (125)$$

$$\left(\frac{\partial (Hm)_G}{\partial [(Hc)_G]_i} \right) = (Hm)_G \cdot \frac{x_i}{(Hc)_G} \quad (126)$$

$$\left(\frac{\partial (Hm)_G}{\partial M_i} \right) = -(Hm)_G \cdot \frac{x_i}{M} \quad (127)$$

These sensitivity coefficients may be inserted into [Formula \(92\)](#), assuming as before the values of $[(Hc)_G]_i$ to be uncorrelated, so as to obtain (after some straightforward algebraic manipulation) the result

$$\left(\frac{u(Hm)_G}{(Hm)_G} \right)^2 = \frac{\sum_{i=1}^N \sum_{j=1}^N \left(\frac{[(Hc)_G]_i}{(Hc)_G} - \frac{M_i}{M} \right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) \cdot \left(\frac{[(Hc)_G]_j}{(Hc)_G} - \frac{M_j}{M} \right)}{\sum_{i=1}^N x_i^2 \cdot u^2 [(Hc)_G]_i + \frac{\sum_{i=1}^N \sum_{j=1}^N x_i \cdot u(M_i) \cdot r(M_i, M_j) \cdot x_j \cdot u(M_j)}{M^2}} \quad (128)$$

This equation is given as ISO 6976:2016, Formula (B.5).