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

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National foreword

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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

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AVA Documents
Document Sharing Hub
Full document details: PD ISO/TR 29922:2017

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

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Documents
Document Sharing Hub
Full document details: PD ISO/TR 29922:2017

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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Documents
Document Sharing Hub
Full document details: PD ISO/TR 29922:2017

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*.

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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	$kJ \cdot mol^{-1}$
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	°C
$u(Y)$	standard uncertainty of Y	(varies)

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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)	$kg \cdot kmol^{-1}$
B	second virial coefficient	$m^3 \cdot mol^{-1}$
C	third virial coefficient	$m^6 \cdot mol^{-2}$
Cp	molar isobaric heat capacity	$kJ \cdot mol^{-1} \cdot K^{-1}$
D	(mass) density	$kg \cdot m^{-3}$
$Đ$	molar density	$mol \cdot m^{-3}$
E	non-random (systematic) bias from the true value of Hc	$kJ \cdot mol^{-1}$
F	function that generates property Y	—
G	relative density	—
Hc	molar-basis calorific value (negative enthalpy of combustion)	$kJ \cdot mol^{-1}$
Hf	enthalpy of formation	$kJ \cdot mol^{-1}$
Hm	mass-basis calorific value	$MJ \cdot kg^{-1}$
Hv	volume-basis calorific value	$MJ \cdot m^{-3}$
J	j-th virial coefficient	$m^{3(j-1)} \cdot mol^{-(j-1)}$
L	molar enthalpy of vaporization of water	$kJ \cdot mol^{-1}$
M	molar mass (molecular weight)	$kg \cdot kmol^{-1}$
N	number of components in a mixture	—
	number of input values of y	—
Q	amount of heat released	$kJ \cdot mol^{-1}$
R	molar gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
S	sum of mole fractions (= 1)	—
T	thermodynamic (absolute) temperature	K
$U(Y)$	expanded uncertainty of Y	(varies)
V	molar volume	$m^3 \cdot mol^{-1}$
W	Wobbe index	$MJ \cdot m^{-3}$
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 Hc	$kJ \cdot mol^{-1}$
μ	dipole moment	debyes
ν	stoichiometric coefficient	—
ξ	relative humidity	—
τ	$100\ K/T$	—
φ	molar amount of saturated exhaust gases per mole of reactant	—

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Symbol	Meaning	Unit
ω	acentric factor	—
$\Lambda_{1\text{-}9}$	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

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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 $(Hc)_G^o$ 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].

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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.*

$$C_aH_bN_cO_dS_e(g) + (a + b/4 - d/2 + e)\ O_2(g) = a\ CO_2(g) + b/2\ H_2O(liq) + c/2\ N_2(g) + e\ SO_2(g) \quad (1)$$

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,

$$[-Hc^o(t)]_j = [-Hc^o(t_0)]_j + \sum_i \int_t^{t_0} v_i \times \left(Cp^o\right)_i \mathrm{d}t \quad (3)$$

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

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 $v_6 = -e$.

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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[7] 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 kJ·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 $\Lambda_{1\text{-}9}$ 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 kJ·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.

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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 $[h^o(25) - h^o(15)]$ are taken directly from tabulations given in Armstrong and Jobe[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 $[h^o(25) - h^o(0)]$ have mostly been calculated using the modified Wilhoit-Harmens formulation[12], as formerly implemented in the computer package GasVLe®.

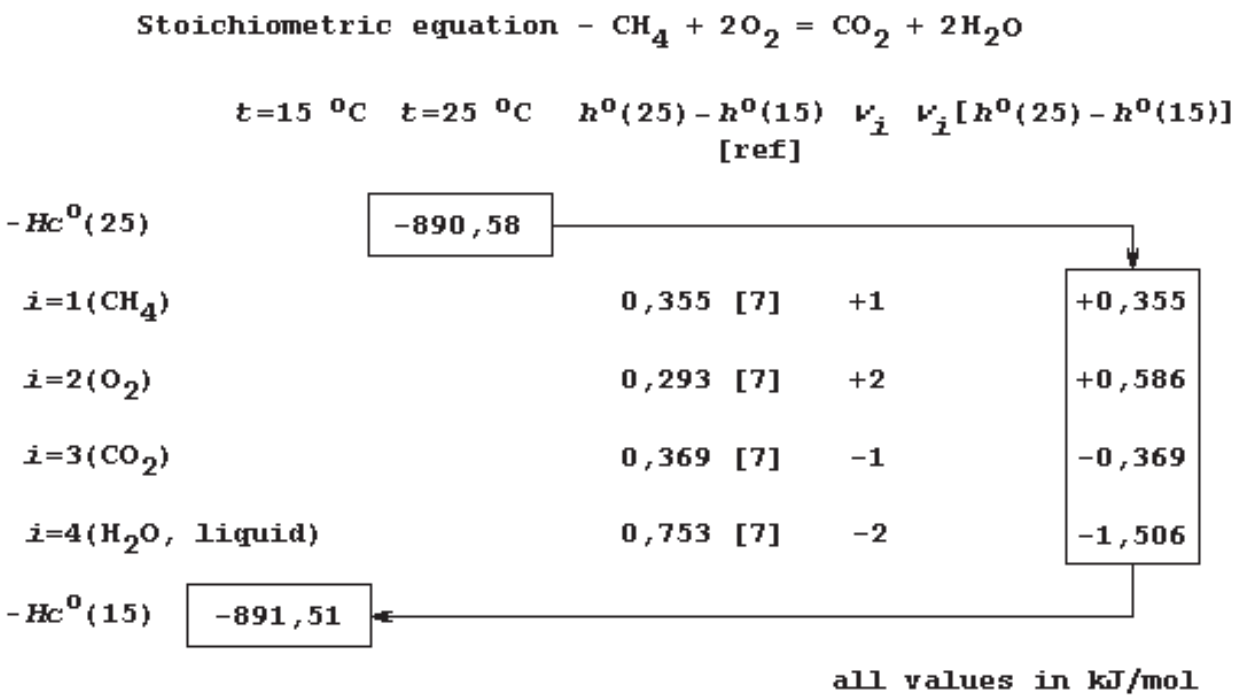

Figure 1 — Conversion of the enthalpy of combustion of the ideal gas from 25 °C to 15 °C — Methane

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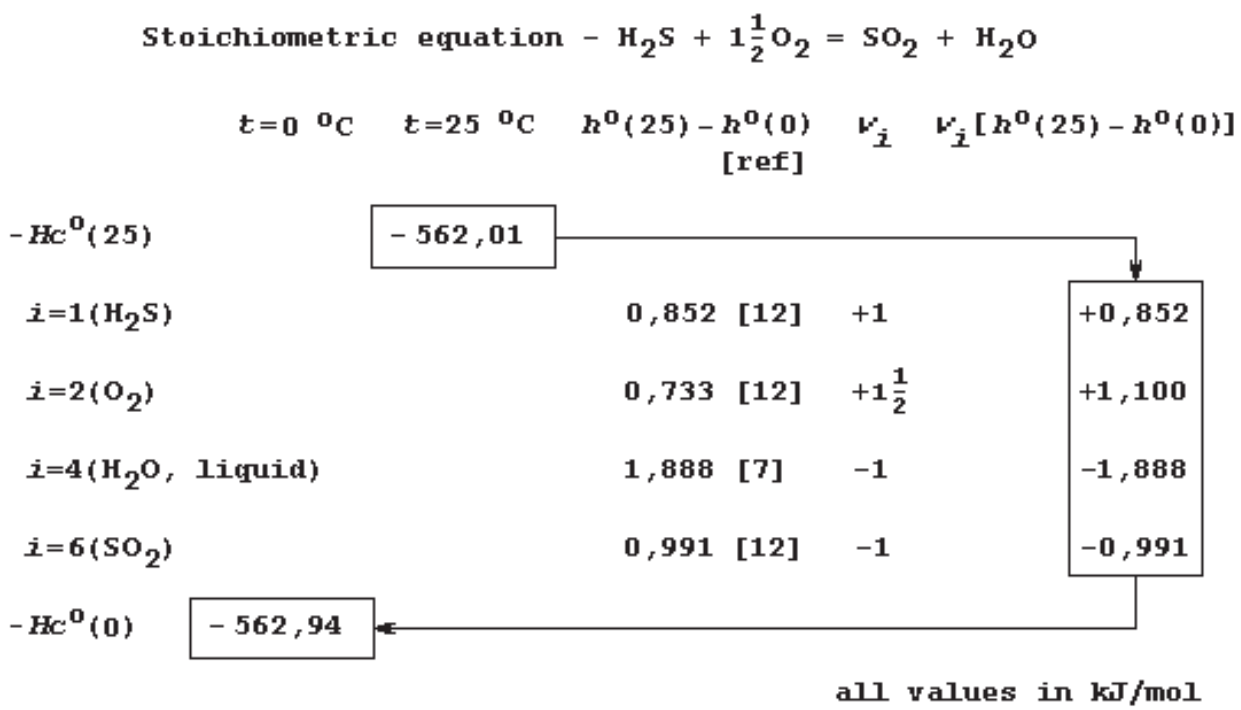

Figure 2 — Conversion of the enthalpy of combustion of the ideal gas from 25 °C to 0 °C — Hydrogen sulfide

5.6 Uncertainty in enthalpy of combustion

The final (right-most) column of ISO 6976:2016, Table 3 lists values for the standard uncertainty $u(Hc^o)$ 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:

a) For methane, see 11.1.4.

b) 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 $U(Hc^o)$ to standard uncertainty $u(Hc^o)$] from the Table A7g column 7 of Armstrong and Jobe[7].

c) For hydrogen, the standard uncertainty $u(Hc^o)$ in the standard enthalpy of combustion is taken as half of the expanded uncertainty $U(Hf^o)$ of the standard enthalpy of formation of water as reported by Rossini[19].

d) For carbon monoxide, the standard uncertainty $u(Hc^o)$ is taken as half the value of $U(Hc^o)$ as reported by Rossini[20].

e) For water, the value of $u(Hc^o)$ is taken as equal to the value of $u(L^o)$ given in ISO 6976:2016, A.4 which, in turn, originates from the work of Wagner and Pruss[3].

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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

$$C_aH_bN_cO_dS_e(g) + (a + b/4 - d/2 + e)\ O_2(g) = a\ CO_2(g) + b/2\ H_2O(liq) + c/2\ N_2(g) + e\ SO_2(g) \quad (5)$$

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 $U(Hf^o)_{O2} = U(Hf^o)_{N2} = 0$, this reduces to

$$u(Hc^o) = 0{,}5 \times \{ [U(Hf^o)_{CHNOS}]^2 + [a \cdot U(Hf^o)_{CO2}]^2 + [(b/2) \cdot U(Hf^o)_{H2O}]^2 + [e \cdot U(Hf^o)_{SO2}]^2 \}^{1/2} \quad (6)$$

where

$U(Hf^o)_{CO2}$ = 0,13 kJ·mol^{-1} (Reference [7])

$U(Hf^o)_{H2O}$ = 0,042 kJ·mol^{-1} (Reference [7]), and

$U(Hf^o)_{SO2}$ = 0,20 kJ·mol^{-1} (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

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

$$C_aH_bN_cO_dS_e(g) + (a + b/4 - d/2 + e)\ O_2(g) = a\ CO_2(g) + b/2\ H_2O(liq) + c/2\ N_2(g) + e\ SO_2(g) \quad (7)$$

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 specfic 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 $\left[(Hc)_G - (Hc)_G^o\right]$, 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

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

where

ν_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 $\nu_1 = 1$ for all j,

b) $i = 2$ for the reactant oxygen, whence $\nu_2 = [a+(b/4)-(d/2)+e]$,

c) $i = 3$ for the product carbon dioxide, whence $\nu_3 = -a$,

d) $i = 4$ for the product water, whence $\nu_4 = -b/2$,

e) $i = 5$ for any product nitrogen, whence $\nu_5 = -c/2$, and

f) $i = 6$ for any product sulfur dioxide, whence $\nu_6 = -e$.

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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[7] that for each reactant or product the enthalpy departure is given by

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

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;

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

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

$$[(Hc)_G - (Hc)_G^o]_j = R \cdot T \times \sum_i \nu_i \cdot \frac{B_i(T) - \left(T \cdot \frac{\mathrm{d}B_i}{\mathrm{d}T}\right)}{V_i(T,p)} \tag{11}$$

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

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

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[7] 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 J·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[7], to show (by manual calculation) that for methane $[(Hc)_G - (Hc)_G^o]$ is about 10 J·mol^{-1}, the calorific value of the real gas being this trivial amount higher than that of the hypothetical ideal gas[26].

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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_2H_6	0,000	0,050
mole fraction C_3H_8	0,000	0,020
mole fraction C_4H_{10}	0,000	0,005
mole fraction C_5H_{12}	0,000	0,002
mole fraction CH_4	0,800	1,000 (calculated by difference)

with, in all cases, $C_2 > C_3 > C_4 > C_5$.

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.

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— at T = 298,15 K $[(Hc)_G - (Hc)_G^o]$ = (0,010 ± 0,001) kJ·mol^{-1}

— at T = 288,15 K $[(Hc)_G - (Hc)_G^o]$ = (0,011 ± 0,001) kJ·mol^{-1}

— at T = 273,15 K $[(Hc)_G - (Hc)_G^o]$ = (0,013 ± 0,001) kJ·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 kJ·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 kJ·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

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

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(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

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

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(real) occupied by one mole of a real gas is often related to V(ideal) through use of the quantity Z, known as the compression factor, such that

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

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

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:

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

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

where V(real), the molar volume, has been abbreviated to V for clarity. The molar volume V is the reciprocal of the molar density $Đ$.

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:

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

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with $B_{jk}(T) = B_{kj}(T)$ (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 $N \cdot (N\text{-}1)/2$ 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 $4 \times [N + N \cdot (N\text{-}1)/2]$ 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(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[7], 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 $x_j, x_k << x_1$ 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.

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Combining Formula (25) with Formula (23) results in

$$Z = 1 + \frac{p}{R \cdot T} \sum_{j}^{N} \sum_{k}^{N} \left(x_j \cdot x_k \right) \times B_{jk} \tag{26}$$

By allowing the further approximation of

$$B_{jk} \approx \sqrt{B_{jj} \cdot B_{kk}} \tag{27}$$

for all *j*,*k*, we then have

$$Z(T, p) = 1 + \frac{p}{R \cdot T} \sum_{j}^{N} \sum_{k}^{N} \left(x_j \cdot x_k \right) \times \sqrt{B_{jj} \cdot B_{kk}} \tag{28}$$

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

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

or

$$Z(T, p) = 1 - \sum_{j}^{N} \sum_{k}^{N} \left(x_j \cdot x_k \right) \times \left[s_j(T, p) \cdot s_k(T, p) \right] \tag{30}$$

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

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

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

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

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

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

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)].

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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

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

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

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

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:

a) truncation of the virial expansion at the two-body interaction (second virial coefficient) term, thereby ignoring the higher order interaction terms [Formula (21)],

b) linearization of the truncated virial equation [Formula (25)], and

c) 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.

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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

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

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,

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

$$\frac{B(T)\cdot p_c}{R\cdot T_c} = (0{,}1445 + 0{,}0637\cdot\omega) - \frac{0{,}330}{T_r} - \frac{(0{,}1385 - 0{,}331\cdot\omega)}{T_r^2} - \frac{(0{,}0121 + 0{,}423\cdot\omega)}{T_r^3} - \frac{(0{,}000607 + 0{,}008\cdot\omega)}{T_r^8} - \frac{(2{,}140\times10^{-4}\cdot\mu_r + 4{,}308\times10^{-21}\cdot\mu_r^8)}{T_r^6} \quad (37)$$

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 τ = 100 K/T and p_2 = 101,325 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 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 $Z(t_2,p_0)$.

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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

j	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

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Table 1 *(continued)*

j	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:

a) values as calculated by the method of 8.1.2 and taken directly from ISO 6976:2016, Table 2;

b) values as calculated by the method of 8.1.1;

c) values given in ISO 6976:1995;

d) values derived, via Formula (31), from values of second virial coefficient calculated using the MGERG formulation as presented in GERG TM-2[35];

e) 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];

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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.

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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 uncertainies) 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]

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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

j	Component	Compression factor $Z(t_2,p_0)$			
		t_2 = 0 °C	t_2 = 15 °C	t_2 = 60 °F	t_2 = 20 °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

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

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

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