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Gas analysis — Conversion of gas mixture composition data

Analyse des gaz — Conversion des données de composition de mélanges gazeux

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 14912 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

The objective of gas analysis is to determine the composition of gas mixtures. Gas mixture composition is expressed qualitatively in terms of specified mixture components of interest, called analytes, and the complementary gas. Gas mixture composition is expressed quantitatively by specifying the amount of every analyte in the mixture and the composition of the complementary gas.

For the purpose of specifying the amount of an analyte in a gas mixture, different quantities are in use. This diversity is due to the fact that in different applications different quantities have decisive advantages. Therefore procedures for conversion between different quantities are required.

In cases where these quantities involve the volumes of the analytes or the gas mixture or both, they depend on the state conditions, i.e. pressure and temperature, of the gas mixture. For each of these quantities, procedures for conversion between different state conditions are required.

As a crude approximation, all of the conversions referred to above can be performed on the basis of the Ideal Gas Law. In most cases, however, an accurate conversion has to take into account the real gas volumetric behaviour of the analyte and of the gas mixture. In particular, many conversions require values of the compression factor (or of the density) of the gas mixture.

This International Standard provides formally exact conversion procedures, based on fundamental principles, which fully account for real gas behaviour of pure gases and gas mixtures. In addition to these, approximate procedures for practical applications are described, designed for different levels of accuracy and available data. These approximations are necessary because measured gas mixture compression factors (or densities) are rarely available and therefore have to be estimated from component data. Uncertainty estimates are given which result from combining approximations in the conversion procedures with the uncertainties of the input data. Where conversions require real-gas volumetric data of pure gases or gas mixtures, these are expressed by compression factors. As equivalents, density data could be converted into compression factor data.

Gas analysis — Conversion of gas mixture composition data

1 Scope

This International Standard defines the following quantities commonly used to express the composition of gas mixtures:

— mole fraction,

— mass fraction,

— volume fraction,

and

— mole concentration,

— mass concentration,

— volume concentration.

For these quantities of composition, this International Standard provides methods for

— conversion between different quantities, and

— conversion between different state conditions.

Conversion between different quantities means calculating the numerical value of an analyte content in terms of one of the quantities listed above from the numerical value of the same analyte content, at the same pressure and temperature of the gas mixture, given in terms of another of these quantities. Conversion between different state conditions means calculating the numerical value of an analyte content, in terms of one of the quantities listed above, under one set of state conditions from the numerical value of the same quantity under another set of state conditions, i.e. pressure and temperature, of the gas mixture. Gas mixture composition can be converted simultaneously between different quantities of composition and different state conditions by combination of the two types of conversion.

This International Standard is applicable only to homogeneous and stable gas mixtures. Therefore any state conditions (pressure and temperature) considered need to be well outside the condensation region of the gas mixture and that of each of the specified analytes (see Annex A).

2 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

NOTE   See also References [1] and [2] in the Bibliography.

2.1 Quantities for the expression of gas mixture composition

NOTE   Further information concerning the terms defined in this subclause is given in 4.1.

2.1.1
mole fraction
amount-of-substance fraction
x
quotient of the amount of substance of a specified component and the sum of the amounts of substance of all components of a gas mixture

NOTE   The mole fraction is independent of the pressure and the temperature of the gas mixture.

2.1.2
mass fraction
w
quotient of the mass of a specified component and the sum of the masses of all components of a gas mixture

NOTE   The mass fraction is independent of the pressure and the temperature of the gas mixture.

2.1.3
volume fraction
ϕ
quotient of the volume of a specified component and the sum of the volumes of all components of a gas mixture before mixing, all volumes referring to the pressure and the temperature of the gas mixture

NOTE   The volume fraction is not independent of the pressure and the temperature of the gas mixture. Therefore the pressure and the temperature have to be specified.

2.1.4
mole concentration
amount-of-substance concentration
c
quotient of the amount of substance of a specified component and the volume of a gas mixture

NOTE   The mole concentration is not independent of the pressure and the temperature of the gas mixture. Therefore the pressure and the temperature have to be specified.

2.1.5
mass concentration
β
quotient of the mass of a specified component and the volume of a gas mixture

NOTE   The mass concentration is not independent of the pressure and the temperature of the gas mixture. Therefore the pressure and the temperature have to be specified.

2.1.6
volume concentration
σ
quotient of the volume of a specified component before mixing and the volume of a gas mixture, both volumes referring to the same pressure and the same temperature

NOTE 1   The volume concentration is not independent of the pressure and the temperature of the gas mixture. Therefore the pressure and the temperature have to be specified.

NOTE 2   The volume fraction (2.1.3) and volume concentration (2.1.6) take the same value if, at the same state conditions, the sum of the component volumes before mixing and the volume of the mixture are equal. However, because the mixing of two or more gases at the same state conditions is usually accompanied by a slight contraction or, less frequently, a slight expansion, this is not generally the case.

2.2   Additional quantities involved in conversions of gas mixture composition

2.2.1
compression factor
Z
quotient of the volume of an arbitrary amount of gas at specified pressure and temperature and the volume of the same amount of gas, at the same state conditions, as calculated from the ideal gas law

NOTE 1   This definition is applicable to pure gases and to gas mixtures, therefore the term "gas" is used as a general term which covers pure gases as well as gas mixtures.

NOTE 2   By definition, the compression factor of an ideal gas is 1. At room temperature and atmospheric pressure, for many gases the compression factor differs only moderately from 1.

2.2.2
mixing factor
f
quotient of the volume of an arbitrary amount of a gas mixture at specified pressure and temperature and the sum of the volumes of all mixture components, before mixing, at the same state conditions

NOTE   If the component volumes are strictly additive, i.e. if the sum of the volumes before mixing is the same as the volume after mixing, the mixing factor is 1. At room temperature and atmospheric pressure, for many gas mixtures the mixing factor differs only slightly from 1.

2.2.3
density
ρ
quotient of the mass of an arbitrary amount of gas and its volume at specified pressure and temperature

NOTE   This definition is applicable to pure gases and to gas mixtures, therefore the term "gas" is used as a general term which covers pure gases as well as gas mixtures.

2.2.4
molar volume
V_{mol}
quotient of the volume of an arbitrary amount of gas at specified pressure and temperature and its amount of substance

NOTE 1   This definition is applicable to pure gases and to gas mixtures, therefore the term "gas" is used as a general term which covers pure gases as well as gas mixtures.

NOTE 2   The amount of substance of a mixture is given by the sum of the amounts of substance of the components.

2.2.5
virial coefficients
coefficients in the expansion of the compression factor in terms of powers of a quantity of state

NOTE   In practice, only two virial expansions are used, where the quantity of state is either the pressure, p, or the inverse molar volume, $1/V_{mol}$, as follows.

$$Z\left(V_{mol},T\right) = 1 + \frac{B(T)}{V_{mol}} + \frac{C(T)}{V_{mol}^2} + \ ...\tag{1}$$

$$Z\left(p,T\right) = 1 + B'(T)\,p + C'(T)\,p^2 + \ ...\tag{2}$$

2.2.5.1
second molar-volume virial coefficient
B
coefficient of $1/V_{\text{mol}}$ in the expansion of the compression factor in terms of inverse powers of the molar volume, V_{mol}

2.2.5.2
third molar-volume virial coefficient
C
coefficient of $1/V_{\text{mol}}^2$ in the expansion of the compression factor in terms of inverse powers of the molar volume, V_{mol}

2.2.5.3
second pressure virial coefficient
B'
coefficient of p in the expansion of the compression factor in terms of powers of the pressure p

2.2.5.4
third pressure virial coefficient
C'
coefficient of p^2 in the expansion of the compression factor in terms of powers of the pressure p

3   Symbols and units

Symbol	Quantity	SI unit
α	abbreviation of $p/(RT)$	mol/m^3
B	second molar-volume virial coefficient	m^3/mol
B'	second pressure virial coefficient	1/Pa
β	mass concentration	kg/m^3
c	mole concentration	mol/m^3
C	third molar-volume virial coefficient	m^6/mol^2
C'	third pressure virial coefficient	1/Pa^2
D	dilution factor	1
f	mixing factor	1
ϕ	volume fraction	1
i	gas mixture components (i = 1, 2, …, N)	—
j, k	gas mixture components (from 1 to N) (where needed in addition to symbol i)	—
m	mass	kg
M	molar mass	kg/mol
n	amount of substance	mol

Symbol	Quantity	SI unit
N	number of gas mixture components	—
p	pressure	Pa
p_{vap}	saturation vapour pressure	Pa
p_{dew}	dew pressure	Pa
R	molar gas constant (8,314 510)	J/(mol·K)
ρ	density	kg/m^3
S	(sample of) gas mixture	—
σ	volume concentration	m^3/m^3
t	Celsius temperature	°C
T	thermodynamic temperature	K
V	volume	m^3
V_{mol}	molar volume	m^3/mol
w	mass fraction	1
W	weight (of a gas cylinder)	kg
x	mole fraction	1
X_{ref}	reference value of state conditions ($X = p, T$)	same as for X
X_{crit}	critical component property ($X = p, T, V, Z$)	same as for X
X_{pscrit}	pseudo-critical mixture property ($X = p, T$)	same as for X
Z	compression factor	1

In addition to the symbols specified above, the following symbols are used to denote objects of generic mathematical expressions.

Symbol	Quantity
F	mathematical function expressing a conversion
I	input quantity of composition
O	output quantity of composition
Ω	conversion factor
K,L,P,Q,Y	general variables or quantities
$\partial F/\partial P$	partial derivative (sensitivity coefficient)
$r(P,Q)$	correlation coefficient of quantities P,Q
$\boldsymbol{R}$	correlation matrix
$u(P)$	standard uncertainty of quantity P
$u^2(P)$	variance of quantity P
$u(P,Q)$	covariance of quantities P,Q
$\boldsymbol{U}$	variance/covariance matrix
$v(P)$	relative standard uncertainty of quantity P

4 Basic principles

4.1 Expression of gas mixture composition

The generic term for the amount of a component in a mixture is "content". This term is intended for use only in a purely descriptive or qualitative sense, and is, without further qualification, inappropriate and insufficient to express quantitatively the amount of a component.

Quantitative statements require the expression of content as a value (the product of a number and a unit) of a "quantity of composition".

For present purposes, six quantities of composition, subdivided into two distinct conceptual families, called fractions and concentrations, are defined in 2.1. The terms "fraction" and "concentration" are themselves incomplete, and cannot be used in quantitative statements of content without qualification by one of the modifiers "mole", "mass" or "volume".

In quantitative expressions of gas mixture composition, the applicable quantity, for example the mole fraction or the mass concentration, shall be used in conjunction with the name or the chemical symbol of the component.

EXAMPLE 1   The hydrogen content in a hydrogen/nitrogen mixture, expressed by mole fraction, is $x(H_2) = 0,1$.

EXAMPLE 2   The sulfur dioxide content in air at 101,325 kPa and 25 °C, expressed by mass concentration, is $\beta(SO_2) = 1$ mg/m^3.

Gas mixture composition may either relate to the preparation of gas mixtures or to the analysis of gas mixtures. In the first case, the composition expresses the formulation of a prepared mixture. Here the components are the parent gases that were mixed. These can be technically pure gases or specified gas mixtures. In the second case, the composition expresses the results of analysis. Here the components are the

analytes (i.e. the distinct chemical substances determined quantitatively) and the matrix (i.e. the complementary gas).

Fractions are often used in the expression of results of gas mixture preparation. If a gas mixture consists of N components, 1, 2, ..., N, and if the amounts of these components in the mixture are quantified by amount of substance, n_1, n_2, ..., n_N, the mole fraction x_i of any component i is given by

$$x_i = \frac{n_i}{\sum_k n_k} \tag{3}$$

If the amounts of the mixture components are quantified by mass, m_1, m_2, ..., m_N, the mass fraction w_i of any component i is given by

$$w_i = \frac{m_i}{\sum_k m_k} \tag{4}$$

If the amounts of the mixture components are quantified by volume, V_1, V_2, ..., V_N, the volume fraction ϕ_i of any component i is given by

$$\phi_i = \frac{V_i}{\sum_k V_k} \tag{5}$$

Concentrations are often used to express the results of mixture analysis. If the amount of a specified analyte, i, found in the analysed sample is quantified by amount of substance, n_i, and if V_S is the sample volume at specified pressure and temperature, the mole concentration (amount-of-substance concentration) c_i is given by

$$c_i = \frac{n_i}{V_S} \tag{6}$$

If the analyte amount is quantified by mass, m_i, the mass concentration β_i is given by

$$\beta_i = \frac{m_i}{V_S} \tag{7}$$

If the analyte amount is quantified by volume, V_i, the volume concentration σ_i is given by

$$\sigma_i = \frac{V_i}{V_S} \tag{8}$$

In all the above expressions, it has to be noted that the sample volume depends on pressure and temperature. In the expression for the volume concentration, the analyte volume also depends on pressure and temperature. For both volumes, the state conditions have to be the same.

The quantities of composition exhibit different behaviour concerning the dependence on pressure and temperature, as follows:

— mole concentration and mass concentration depend strongly on state conditions,

— volume fraction and volume concentration depend weakly on state conditions,

— mole fraction and mass fraction are strictly independent of state conditions.

The quantities above are primarily intended for describing the composition of gas mixtures which are homogeneous and stable. In a technical sense, they may also apply to both heterogeneous and unstable mixtures but that is not their intended usage in this International Standard (see below).

Given the restriction to homogeneous gas mixtures, the main implication for this International Standard is that the state conditions (pressure and temperature) shall be such that the mixture is completely gaseous. This requirement applies to all the quantities. In addition,

a)   the volume concentration is only applicable if the state conditions are such that the individual component under consideration, before mixing, is completely gaseous, and

b)   the volume fraction is only applicable if the state conditions are such that all components, before mixing, are completely gaseous.

The expression "completely gaseous" means, for an individual component, that the pressure is well below the saturation pressure at the given temperature or that the temperature is well above the critical temperature. For a mixture, the equivalent condition is that the pressure is well below the dew pressure at the given temperature or that the temperature is well above the cricondentherm. In other words, the state conditions are to be well outside the relevant condensation regions. Methods for assessing whether, at specified state conditions, gas mixtures and their components are completely gaseous are described in Annex A.

If the restriction to homogeneous and stable mixtures cannot be guaranteed, then the way forward is inevitably complex. For instance, if the gas mixture is not stable at the relevant state conditions, i.e. if chemical reactions between mixture components take place, then the composition depends upon time and shall be described accordingly (either using time-averaged quantities or a functional dependence upon time). Analogously, in the case of a heterogeneous gas mixture, either spatial distributions or spatial averages shall be employed. Situations of this sort, however, are beyond the scope of this International Standard.

4.2   Conversion between different quantities

The conversion between different quantities of composition uses the basic relations between the following quantities, which apply both to pure gases and to gas mixtures:

⎯   amount of substance, n

⎯   mass, m

⎯   volume, V

The relation between amount of substance and mass is given by Equation (9)

$$n = \frac{m}{M} \tag{9}$$

where M is the molar mass of the gas or gas mixture.

The molar masses of pure gases are calculated from the molar masses of the elements (see 7.1.1). The molar masses of gas mixtures are calculated from the composition and the molar masses of the components (see 7.2.1).

The relation between amount of substance and volume is given by Equation (10).

$$n = \frac{pV}{ZRT} \tag{10}$$

where

p is the pressure of the gas or gas mixture;

T is the temperature of the gas or gas mixture;

Z is the compression factor of the gas or gas mixture;

R is the molar gas constant.

Equation (10) is the general equation of state for real gases. The compression factors of pure gases can be calculated approximately from tabulated virial coefficients (see 7.1.2). The compression factors of gas mixtures can be calculated approximately from the composition and the virial coefficients of the components (see 7.2.2).

The relation between mass and volume is given by Equation (11):

$$m = \rho V \tag{11}$$

where ρ is the density of the gas or gas mixture.

The three quantities M, Z and ρ can be related by combining Equations (9), (10) and (11) to give

$$\rho Z = \frac{Mp}{RT} \tag{12}$$

Therefore, only two of these quantities are independent. In this International Standard, the conversion between quantities of composition is based on known values of M and Z.

In addition to the equations above, conversions between fractions and concentrations require relations between the amount of a gas mixture and the amounts of its components.

If a gas mixture sample S consists of N components, 1, 2, ..., N, the amount of substance n_S of the gas mixture sample is given by the sum of the amounts of substance of the components.

$$n_S = \sum_k n_k \tag{13}$$

Analogously, the mass m_S of the gas mixture sample is given by the sum of the component masses.

$$m_S = \sum_k m_k \tag{14}$$

While amounts of substance and masses of mixture components are strictly additive, for component volumes additivity is only an approximation (though usually very good). The relation between the volume V_S of the gas mixture sample and the component volumes at identical state conditions is as follows:

$$V_S = f_S \sum_k V_k \tag{15}$$

where f_S is the mixing factor of the gas mixture S.

In the majority of applications, the mixing factor can be taken as unity (see 7.2.3).

4.3   Conversion between different state conditions

If gas mixture composition is expressed in terms of quantities which depend on pressure and temperature, reference conditions are necessary for comparison purposes. Therefore, procedures for converting any such mixture composition from given state conditions to specified reference conditions are required. The basic relation involved in these conversions is the relation between the volume $V(p,T)$ of a sample of a gas or gas

mixture at given state conditions (p, T) and the volume $V(p_{\text{ref}}, T_{\text{ref}})$ of the same sample at specified reference conditions $(p_{\text{ref}}, T_{\text{ref}})$, using Equation (10).

$$\frac{V(p,T)}{V(p_{\text{ref}}, T_{\text{ref}})} = \frac{p_{\text{ref}} T Z(p,T)}{p T_{\text{ref}} Z(p_{\text{ref}}, T_{\text{ref}})} \tag{16}$$

5 Main procedures

5.1 Conversion between different quantities of composition

5.1.1 Conversion of specified analyte contents

Conversion between different quantities of composition refers to specified state conditions (pressure p, temperature T) of the gas mixture under consideration. Conversion is performed by multiplication with a conversion factor which in most cases is a quotient, composed of one or several quantities of the component i under consideration and the gas mixture S. For example, mole concentrations c_i are converted into mass fractions w_i as follows:

$$w_i = \frac{RTZ_S}{pM_S} M_i c_i \tag{17}$$

where

M_i and M_S are the molar masses of component i and mixture S;

Z_S is the compression factor of mixture S at the specified state conditions of p and T.

Depending on which two of the three dependent quantities molar mass, M, compression factor, Z, and density, ρ, are selected, the conversion factors can be expressed differently. In this International Standard, conversion factors are always expressed in terms of M and Z. To utilize density data of pure gases and gas mixtures, these would be converted into compression factor data according to Equation (12).

In Clause 7, the determination of the input quantities required for conversions is addressed.

Except for conversion between mole fractions and mass fractions, conversion between different quantities of composition is only applicable if the state conditions (pressure and temperature) considered are well outside the condensation region of the gas mixture as well as of each of the components. Otherwise grossly erroneous or misleading results are liable to occur. For example, if one of the components is not completely gaseous under the state conditions considered, then the content of this component cannot be specified by volume fraction or by volume concentration (see 2.1).

Table 1 specifies a complete set of conversion factors, expressed in terms of molar masses and compression factors of the component and the mixture under consideration. To obtain a desired quantity, take a given quantity and multiply it by the corresponding factor in Table 1.

Table 1 — Conversion factors between quantities of composition

Desired quantity	Given quantity x_i	Given quantity ϕ_i	Given quantity w_i	Given quantity c_i	Given quantity σ_i	Given quantity β_i
x_i	1	$\dfrac{Z_S}{f_S Z_i}$	$\dfrac{M_S}{M_i}$	$\dfrac{Z_S}{\alpha}$	$\dfrac{Z_S}{Z_i}$	$\dfrac{Z_S}{\alpha M_i}$
ϕ_i	$\dfrac{f_S Z_i}{Z_S}$	1	$\dfrac{f_S M_S Z_i}{Z_S M_i}$	$\dfrac{f_S Z_i}{\alpha}$	f_S	$\dfrac{f_S Z_i}{\alpha M_i}$
w_i	$\dfrac{M_i}{M_S}$	$\dfrac{Z_S M_i}{f_S M_S Z_i}$	1	$\dfrac{Z_S M_i}{\alpha M_S}$	$\dfrac{Z_S M_i}{M_S Z_i}$	$\dfrac{Z_S}{\alpha M_S}$
c_i	$\dfrac{\alpha}{Z_S}$	$\dfrac{\alpha}{f_S Z_i}$	$\dfrac{\alpha M_S}{Z_S M_i}$	1	$\dfrac{\alpha}{Z_i}$	$\dfrac{1}{M_i}$
σ_i	$\dfrac{Z_i}{Z_S}$	$\dfrac{1}{f_S}$	$\dfrac{M_S Z_i}{Z_S M_i}$	$\dfrac{Z_i}{\alpha}$	1	$\dfrac{Z_i}{\alpha M_i}$
β_i	$\dfrac{\alpha M_i}{Z_S}$	$\dfrac{\alpha M_i}{f_S Z_i}$	$\dfrac{\alpha M_S}{Z_S}$	M_i	$\dfrac{\alpha M_i}{Z_i}$	1

x_i	is the mole fraction of component i	M_i	is the molar mass of component i
ϕ_i	is the volume fraction of component i	Z_i	is the compression factor of component i
w_i	is the mass fraction of component i	M_S	is the molar mass of gas mixture S
c_i	is the mole concentration of component i	Z_S	is the compression factor of gas mixture S
σ_i	is the volume concentration of component i	f_S	is the mixing factor of gas mixture S
β_i	is the mass concentration of component i	α	is the abbreviation of the quotient $p/(RT)$

NOTE   All quantities refer to the specified state conditions (pressure p, temperature T) of the gas mixture under consideration.

5.1.2   Conversion of complete compositions

If the composition for a gas mixture is completely known, that is, if the content of all mixture components including the complementary gas is available, then the conversion factors may be largely reduced to component quantities. This is done by means of summation relations, expressing single or compound mixture quantities as sums over component quantities, for example as follows:

$$\frac{Z_S}{f_S} = \sum_k x_k Z_k \tag{18}$$

and

$$M_S = \sum_k x_k M_k \tag{19}$$

If the task is to convert mole fractions into another quantity of composition, and if the complete molar composition of the gas mixture under consideration is available, then Equations (18) and (19) may be utilized to express any required conversion factor in terms of component data, i.e. mole fractions x_k, molar masses M_k and compression factors Z_k. As an exception, the mixing factor f_S cannot be expressed in terms of component data and has to be estimated separately.

Table 2 specifies conversion factors, designed for conversion of complete composition data, based on summation relations for mixture quantities. The relevant summation relations are given in Annex B. The given composition shall be specified in term of fractions, while the desired composition could be expressed in fractions or in concentrations. To obtain a desired quantity, take a given quantity and multiply by the corresponding factor in Table 2.

In principle, this approach is also applicable to conversion of complete compositions expressed in concentrations. However, the application range of such conversions is restricted to specialized cases, since concentrations are normally not used for expressing complete compositions. Therefore conversions of this kind are not considered in this International Standard. Tables for conversion of concentrations into fractions based on summation relations can be found in DIN 51896-1[18].

Table 2 — Conversion factors between quantities of composition,
based on summation relations, using component compression factors

Desired quantity	Given quantity x_i	Given quantity ϕ_i	Given quantity w_i
x_i	1	$\dfrac{1/Z_i}{\sum \phi_k/Z_k}$	$\dfrac{1/M_i}{\sum w_k/M_k}$
ϕ_i	$\dfrac{Z_i}{\sum x_k Z_k}$	1	$\dfrac{Z_i/M_i}{\sum w_k Z_k/M_k}$
w_i	$\dfrac{M_i}{\sum x_k M_k}$	$\dfrac{M_i/Z_i}{\sum \phi_k M_k/Z_k}$	1
c_i	$\dfrac{\alpha}{f_S \sum x_k Z_k}$	$\dfrac{\alpha}{f_S Z_i}$	$\dfrac{\alpha/M_i}{f_S \sum w_k Z_k/M_k}$
σ_i	$\dfrac{Z_i}{f_S \sum x_k Z_k}$	$\dfrac{1}{f_S}$	$\dfrac{Z_i/M_i}{f_S \sum w_k Z_k/M_k}$
β_i	$\dfrac{\alpha M_i}{f_S \sum x_k Z_k}$	$\dfrac{\alpha M_i}{f_S Z_i}$	$\dfrac{\alpha}{f_S \sum w_k Z_k/M_k}$

$x_i\,(x_k)$ is the mole fraction of component $i\,(k)$

$\phi_i\,(\phi_k)$ is the volume fraction of component $i\,(k)$

$w_i\,(w_k)$ is the mass fraction of component $i\,(k)$

c_i is the mole concentration of component i

σ_i is the volume concentration of component i

β_i is the mass concentration of component i

$M_i\,(M_k)$ is the molar mass of component $i\,(k)$

$Z_i\,(Z_k)$ is the compression factor of component $i\,(k)$

f_S is the mixing factor of gas mixture S

α is the abbreviation of the quotient $p/(RT)$

NOTE   All quantities refer to the specified state conditions (pressure p, temperature T) of the gas mixture under consideration.

5.2 Conversion to reference conditions

Amongst the six quantities of composition considered in this International Standard, only the mole fraction and the mass fraction are independent of the state conditions (pressure and temperature) of the gas mixture. In contrast to this, the value of the volume fraction, the mole concentration, the mass concentration or the volume concentration of a component varies with changes of pressure and temperature. The extent of variation depends on the extent of such changes, the nature of the gas, and the quantity under consideration (see 4.1).

Conversion of these quantities from given state conditions (p,T) to specified reference conditions (p_{ref}, T_{ref}) is performed by multiplication with a conversion factor as follows:

$$c_i\left(p_{ref}, T_{ref}\right) = \frac{p_{ref} T Z_S\left(p,T\right)}{p T_{ref} Z_S\left(p_{ref}, T_{ref}\right)} c_i\left(p,T\right) \tag{20}$$

$$\beta_i\left(p_{ref}, T_{ref}\right) = \frac{p_{ref} T Z_S\left(p,T\right)}{p T_{ref} Z_S\left(p_{ref}, T_{ref}\right)} \beta_i\left(p,T\right) \tag{21}$$

$$\sigma_i\left(p_{ref}, T_{ref}\right) = \frac{Z_S\left(p,T\right) Z_i\left(p_{ref}, T_{ref}\right)}{Z_S\left(p_{ref}, T_{ref}\right) Z_i\left(p,T\right)} \sigma_i\left(p,T\right) \tag{22}$$

$$\phi_i\left(p_{ref}, T_{ref}\right) = \frac{f_S\left(p_{ref}, T_{ref}\right) Z_S\left(p,T\right) Z_i\left(p_{ref}, T_{ref}\right)}{f_S\left(p,T\right) Z_S\left(p_{ref}, T_{ref}\right) Z_i\left(p,T\right)} \phi_i\left(p,T\right) \tag{23}$$

Instead of using Equations (20) to (23), conversion to other state conditions could be performed using mole fractions or mass fractions.

Conversion to reference conditions is only applicable if the reference conditions under consideration, pressure and temperature, are well outside of the condensation region of the gas mixture as well as of each of the components. Otherwise grossly erroneous or misleading results are liable to occur. For example, if one of the components is not completely gaseous under the reference conditions considered, then the content of this component cannot be specified by volume fraction or by volume concentration (see 2.1).

6 Practical implementation

6.1 Conversion between quantities of composition

The factors by which different quantities of composition are mutually interconverted can include data for the component i under consideration (the molar mass M_i, the compression factor Z_i) and data for the entire mixture S (the molar mass M_S, the compression factor Z_S, the mixing factor f_S).

If the component and mixture data are available as required, the application of the factors specified in 5.1.1, Table 1 is straightforward. In practice component compression factors will often not be available at the state conditions (pressure p, temperature T) under consideration. In this case, these quantities will have to be calculated from available data, using for example virial coefficients (see 7.1).

The main problem, however, is the lack of gas mixture data. With the exception of air, which for practical purposes can be treated like a well-characterized pure gas, neither the molar mass nor the required volumetric properties (compression factor, mixing factor) of the gas mixture will usually be available, and measurement of these data will not be practical. To overcome these problems, this International Standard considers the following two main alternatives.

a) If the composition of the gas mixture is specified completely by mole fractions, mass fractions or volume fractions, the relevant combinations of mixture property data required for conversion into other quantities of composition can be expressed almost completely by weighted averages of component property data.

Using these summation rules, conversion of fractions into other fractions or concentrations can be performed using the conversion factors specified in Table 2. The input required for these conversions is:

— complete mixture composition data,

— relevant component property data,

— an estimate of the mixing factor (only for conversion into concentrations).

These procedures will normally be applied in the case of synthetic mixtures, where the complete composition is available from the mixture preparation formulation. Additional details for conversions of this type are specified in 6.3.

Mixture components can be pure gases and specified gas mixtures. For example, as dry air is a well characterized gas with known molar mass and compression factor, a calibration gas mixture of SO_2 in dry air is conveniently treated as a 2-component mixture instead of a mixture of SO_2, N_2, O_2, Ar, CO_2 etc.

b) If the composition of the gas mixture is not specified completely, the strategy for estimating conversion factors depends on the mixture property data involved, the target conversion uncertainty and the available information on mixture composition. These procedures will normally be applied in the case of analysed mixtures, where most often only specified analytes have been determined quantitatively, while the composition of the complementary gas (matrix) is less well known.

Additional details for conversions of this type are specified in 6.2.

Even if the composition of a gas mixture is not known completely, it can be expressed as a mixture consisting of the specified analytes and a semi-quantitatively specified matrix. Then the conversion procedure according to a) can be used, where the relevant property data of the matrix are estimated with appropriate uncertainty from available information.

Procedures for conversion between different state conditions are addressed in 6.4.

6.2 Conversion of single analyte contents

When the task is to convert single analyte contents, and complete mixture composition data are not available, then the appropriate conversion factor in Table 1 needs to be selected. Next, the constituents of the conversion factor are examined as to whether appropriate data are available or can be estimated using available information as follows.

— For M_i, the molar mass of the specified analyte, take the value from an acknowledged reference or calculate it according to 7.1.1.

— For Z_i, the compression factor of the specified analyte at specified state conditions (p,T), which is normally not available in published data compilations, calculate the value from tabulated virial coefficients according to 7.1.2.

— For M_S, the molar mass of the gas mixture, which is normally not available in published data compilations, the calculation from the composition requires complete and accurate composition data. In absence of these, estimation is only possible in special cases such as traces of analytes in a pure balance gas, using procedures from 7.2.1.

— For Z_S, the compression factor of the gas mixture at specified state conditions (p,T), which is normally not available in published data compilations, calculate the value from tabulated virial coefficients and composition data according to 7.2.2, or use the simple approximations specified in 7.3.

— For f_S, the mixing factor of the gas mixture at specified state conditions (p,T), which is normally not available in published data compilations, the value generally can be taken as unity except for special cases (strong interactions). See 7.2.3.

— For α, the quotient $p/(RT)$, the value is known.

In summary, in the absence of complete and accurate mixture composition data, conversions involving the molar mass of the mixture cannot be undertaken except in special cases. Conversion involving the compression factor and/or the mixing factor of the gas mixture can be performed, using simple estimates which do not require detailed mixture composition data.

6.3 Conversion of complete compositions

When complete mixture composition data in mole fractions, mass fractions or volume fractions are available, and if the task is to express any of these in terms of another quantity of composition, the required conversion factor in Table 2 is identified. Next, the constituents of the conversion factor are examined as to whether appropriate data are available or can be estimated using available information. Besides the composition data, these data will be obtained as follows.

— For M_i (M_k), the molar mass of the specified analyte and other components, take the value from an acknowledged reference or calculate it according to 7.1.1.

— For Z_i (Z_k), the compression factor of the specified analyte and other components, which is normally not available in published data compilations, calculate the value from tabulated virial coefficients according to 7.1.2.

— For f_S, the mixing factor of the gas mixture, which is normally not available in published data compilations, the value generally can be taken as unity except for special cases (strong interactions).

— For α, the quotient $p/(RT)$, the value is known.

6.4 Conversion between state conditions

Conversion between different state conditions mainly requires compression factor data for the component under consideration and for the entire mixture at the specified state conditions. As for conversion between different quantities of composition, the main problem is the lack of gas mixture data, and the strategies specified in 6.2 and 6.3 for handling these problems are also applicable to conversion between state conditions. Since the molar mass of the gas mixture is not involved, problems related to the estimation of this quantity in absence of complete and accurate composition data are not encountered for such conversions.

6.5 Simple approximations applicable to conversion

6.5.1 Ideal mixture of ideal gases

An ideal mixture of ideal gases is characterized by the following conditions:

— unity mixing factor $\qquad f_S = 1$;

— unity component compression factors $\qquad Z_i = 1$.

As a consequence, the mixture compression factor equals unity, too, i.e. $Z_S = 1$. This, in turn, implies that component mole fractions, volume fractions and volume concentrations take the same values, i.e. $x_i = \phi_i = \sigma_i$.

The model of an ideal mixture of ideal gases may be applied to all gas mixtures and provides a useful first approximation. For gas mixtures containing condensable components, the level of conversion error due to this approximation is typically 1 % relative. For mixtures of permanent gases, this conversion error can be much less.

6.5.2 Ideal mixture of real gases

An ideal mixture of real gases is characterized by the following condition:

— unity mixing factor $\qquad f_S = 1$

This implies that component volume fractions and volume concentrations take the same values, i.e. $\phi_i = \sigma_i$.

The model of an ideal mixture of real gases may be applied to all gas mixtures. In almost all cases, it can be expected to provide an accurate approximation that is sufficient for every practical purpose. Exceptions are gas mixtures with strong intermolecular forces such as azeotropic mixtures. For other gas mixtures, the level of conversion error due to this approximation is typically 0,3 % relative.

6.5.3   Trace gas mixture

A trace gas mixture consists of a complementary gas 1, and a number of components 2, 3, …N, all of which are only present in small amounts. Therefore the compression factor, density and molar mass of the mixture are approximately given by those of the complementary gas, i.e. $Z_S = Z_1$, $\rho_S = \rho_1$, $M_S = M_1$. Furthermore, the mixing factor may be taken as unity, i.e. $f_S = 1$.

For mixtures where the content of the complementary gas is above 90 %, the level of conversion uncertainty due to this approximation is typically 0,5 %, except for conversions involving mass fractions.

7   Input quantities and their uncertainties

7.1   Pure gas data

7.1.1   Molar mass

The molar mass of a pure gas is calculated from the molar masses of the elements according to its molecular formula. The molar masses of the elements shall be taken from the most recent IUPAC compilation (see Reference [6] for the current version).

NOTE   In the IUPAC compilation, the molar masses of the elements are referred to as "atomic weights".

The standard uncertainty of the molar mass of a pure gas is calculated from the standard uncertainties of the molar masses of the elements concerned as the positive square root of the corresponding sum of squares (see Reference [3]).

As an example, for a pure gas with molecular formula $A_a B_b C_c$ the molar mass M and its standard uncertainty $u(M)$ are given as follows:

$$M = aM_A + bM_B + cM_C \tag{24}$$

$$u^2(M) = a^2 u^2(M_A) + b^2 u^2(M_B) + c^2 u^2(M_C) \tag{25}$$

where

M_A, M_B, M_C are the molar masses of elements A, B, C, respectively;

$u(M_A)$, $u(M_B)$, $u(M_C)$ are the standard uncertainties of M_A, M_B, M_C, respectively.

Information on the uncertainty of the molar mass of elements is given in References [6] and [7]. For the most common elements occurring in gases, such as H, He, C, N, O, F, Ne, S and Cl, the relative standard uncertainty of the molar mass is about 10^{-4} or less and for the molar mass of the most common pure gases the relative standard uncertainty is of the same order of magnitude.

A compilation of molar masses, including uncertainty, for gases and liquids occurring as specified components of gas mixtures is given in Annex C.

7.1.2 Compression factor

For most pure gases, the compression factor at room temperature and atmospheric pressure differs only moderately from unity. For pure gases occurring as natural gas constituents, compression factor data at common reference conditions (101,325 kPa, 0 °C and 15 °C) are given in References [8] and [9]. Reference [10] contains an extensive compilation of compression factor data for gases at normal reference conditions (101,325 kPa, 0 °C). A related compilation of compression factors for gases at 100 kPa and 15 °C, calculated from virial coefficient data in Reference [10], is given in Annex C.

Information on the uncertainty of tabulated compression factor data may be obtained from the number of significant digits specified. For details, the references should be consulted on their rounding procedure.

For estimating the compression factor of a pure gas at state conditions far outside the condensation region, the most important tool is the truncated virial expansion, using tabulated virial coefficients. This is because compression factors, if available at all in gas data compilations, are most often tabulated for selected reference conditions only. If, for the state conditions under consideration, compression factor data are not available, they can be calculated approximately from second pressure virial coefficient data, using Equation (2) truncated after the linear term:

$$Z(p,T) = 1 + B'(T)p \tag{26}$$

where

$Z(p,T)$ is the compression factor at pressure p and temperature T;

$B'(T)$ is the second pressure virial coefficient at temperature T.

Equation (26) is applicable at state conditions where the density of the gas is less than 50 % of its critical density (see Reference [11]).

In the temperature range between 0 °C and 30 °C, the virial coefficient $B'(T)$ can be calculated approximately by linear interpolation as follows:

$$B'(T) = B'_0 + (B'_{30} - B'_0)\frac{t}{30} \tag{27}$$

where

t is the temperature, expressed in degrees Celsius, corresponding to T, the temperature expressed in kelvins;

B'_0 is the second pressure virial coefficient at 0 °C;

B'_{30} is the second pressure virial coefficient at 30 °C.

Annex C contains an extensive compilation of second pressure virial coefficients at 0 °C and 30 °C taken from Reference [10]. In Reference [12], among others, a large body of experimental gas data has been compiled in the format of parameters of empirical equations by which second molar-volume virial coefficients $B(T)$ can be calculated approximately over specified temperature ranges. Other sources of molar-volume virial coefficient data are References [9] and [13].

For use in Equation (26), molar-volume virial coefficients $B(T)$ have to be converted to pressure virial coefficients $B'(T)$ as follows:

$$B'(T) = \frac{B(T)}{RT} \tag{28}$$

For compression factor calculations using Equation (26), the uncertainty due to truncation of the virial expansion can be estimated as follows. According to Reference [11], the compression factor lies between the approximate values obtained from Equations (1) and (2), respectively, both truncated after the linear term. Assuming this, the maximum error of Z calculated by Equation (26) is $(1 - Z)^2/Z$. Through division by $\sqrt{3}$ this maximum error is converted to a standard uncertainty (the standard deviation of a rectangular distribution between the error bounds).

EXAMPLE   For Z = 0,9, the maximum relative error is about 1 % and the relative standard uncertainty is 0,6 %. For Z = 0,95, the maximum relative error and the relative standard uncertainty are reduced to 0,25 % and 0,15 %, respectively. At state conditions well outside the condensation region compression factors below 0,95 are exceptional.

For interpolation of virial coefficient data using Equation (27), the uncertainty due to lack of linearity can be estimated on the basis of empirical studies (see Reference [10]) in which the interpolation error was found to be at most 2 % relative. Through division by $\sqrt{3}$, this maximum relative error is converted to a relative standard uncertainty of 1,2 %.

Conversion of molar-volume virial coefficients to pressure virial coefficients using Equation (28) does not introduce any additional uncertainty.

The overall standard uncertainty of compression factor data determined according to this clause is calculated by combining the standard uncertainties on the input data and the standard uncertainties due to the approximation procedures involved, as the positive root of the corresponding sum of squares (see Reference [3]). For example, if compression factors $Z(p,T)$ are calculated from virial coefficients B'_0 and B'_{30} according to Equations (26) and (27), the overall uncertainty is given by combination of

a)   the uncertainty due to truncation [Equation (26)],

b)   the uncertainty due to interpolation [Equation (27)],

c)   the uncertainty of the input virial coefficient data,

as follows:

$$u^2\left(Z\right) = p^2 u^2\left(B'\right) + \frac{\left(1-Z\right)^4}{3Z^2} \tag{29}$$

where

$$u^2\left(B'\right) = \left(0{,}012\right)^2 B'^2 \frac{t\left(30-t\right)}{\left(15\right)^2} + u^2\left(B'_{\mathrm{dat}}\right) \tag{30}$$

In Equation (30), the first term on the right-hand side is the uncertainty contribution due to interpolation errors, which was estimated above as 1,2 % relative at the maximum, assumed to occur at midrange, t = 15 °C, and decreasing towards boundaries, 0 °C and 30 °C. The second term, $u^2\left(B'_{\mathrm{dat}}\right)$ accounts for the average uncertainty of the virial coefficient data B'_0 and B'_{30}.

NOTE   As a rule, estimates of B'_0 and B'_{30} have at least 80 % of error in common. Therefore a joint average uncertainty is used in Equation (30).

For the virial coefficient data in Annex C, a rough estimate of the average uncertainty $u^2\left(B'_{\mathrm{dat}}\right)$ of the virial coefficient data B'_0 and B'_{30} is also given.

7.2 Gas mixture data

7.2.1 Molar mass

For conversion of complete compositions according to 6.3, the molar mass of the mixture under consideration is not required. This subclause therefore refers to conversion of single analyte contents according to 6.2, as far as estimation of molar masses from available information on mixture composition is concerned.

Molar masses of gas mixtures have only been tabulated in exceptional cases, for example for dry air (see References [8] and [10]). Therefore, as a rule, the molar mass of a gas mixture has to be calculated or estimated on the basis of information on its composition.

The molar mass of a gas mixture can be calculated from its molar composition and from the molar masses of the components according to Equation (31).

$$M_S = \sum_{i=1}^{N} x_i M_i \tag{31}$$

The standard uncertainty on an estimate of the molar mass of a given mixture from composition data of limited accuracy is obtained by uncertainty propagation on Equation (31) from the standard uncertainties of the component molar masses and from those of the component mole fractions. How this is done in detail depends on the error structure of the composition of the gas mixture. The most usual case is that the gas mixture contains a balance component N, whose mole fraction is determined by difference, while the mole fractions of the other components are determined independently. Equation (31) can then be rearranged by elimination of the mole fraction of the balance gas as follows:

$$M_S = M_N + \sum_{i=1}^{N-1} x_i \left(M_i - M_N \right) \tag{32}$$

In this case, the standard uncertainty of the molar mass of the gas mixture is given by

$$u^2(M_S) = \left(1 - \sum_{i=1}^{N-1} x_i \right)^2 u^2(M_N) + \sum_{i=1}^{N-1} x_i^2 u^2(M_i) + \sum_{i=1}^{N-1} (M_i - M_N)^2 u^2(x_i) \tag{33}$$

In other cases, for example if all components were determined independently, and the raw mole fractions were normalized to unity, the correlation of errors in composition data has to be taken into account by inclusion of covariance terms in calculating the uncertainty (see 8.3 and 8.4 for procedures and Annex D, Example 2 for an example).

Most often, in Equation (33), the last term, associated with the uncertainty on the composition data is the dominant contribution, and the other terms, associated with the uncertainty on the molar masses of pure gases can be neglected.

If the composition of the gas mixture under consideration is given in mass fractions or volume fractions, the molar mass of the mixture can be calculated from the component molar masses using the appropriate summation relation from Annex B. For instance, if the composition is given in mass fractions, the molar mass of the mixture is calculated as follows:

$$\frac{1}{M_S} = \sum_{i=1}^{N} \frac{w_i}{M_i} \tag{34}$$

The uncertainty analysis for this calculation follows the same principles as those for calculations on a molar composition basis.

If the available information on the composition of the gas mixture under consideration involves concentrations, these may be converted into appropriate fractions using the ideal-gas approximation according to 6.5.1, which are then used to estimate the molar mass of the mixture.

7.2.2 Compression factor

For conversion of complete compositions according to 6.3, the compression factor of the mixture under consideration is not required. This subclause therefore refers to conversion of single analyte contents according to 6.2, as far as estimation of compression factors from available information on mixture composition is concerned.

Compression factor data of gas mixtures have only been tabulated in exceptional cases, for example for dry air (see References [8] and [10]). Therefore, as a rule, the compression factor of a gas mixture has to be calculated or estimated on the basis of information on its composition.

The compression factor of a gas mixture can be calculated from its molar composition and from the compression factors of the components according to Equation (35).

$$Z_S = f_S \sum_{i=1}^{N} x_i Z_i \tag{35}$$

In Equation (35), it is understood that all quantities, which depend on the state conditions, refer to the specified pressure p and the specified temperature T of the gas mixture.

Unless specific information is available, the mixing factor of a gas mixture is taken as unity (see 7.2.3). Then Equation (35) can be reduced to an equivalent of Amagat's Law.

$$Z_S = \sum_{i=1}^{N} x_i Z_i \tag{36}$$

The standard uncertainty of mixture compression factors calculated by Equation (36) is obtained by combination of

a) the uncertainty due to the error in approximating the mixing factor by unity,

b) the uncertainty of the component compression factors, and

c) the uncertainty of the component mole fractions.

The uncertainty related to approximating the mixing factor by unity is given by (see 7.2.3)

$$u_{\text{mix}}^2 (Z_S) = \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i^2 x_j^2 \left(Z_i - Z_j \right)^2 \tag{37}$$

The other contributions b) and c) to the calculation of uncertainty associated with Equation (36) are calculated in a manner similar to that used in 7.2.1.

Except for standard reference conditions, where tabulated component compression factors may be available, Equation (36) will be combined with the truncated virial expansion of component compression factors according to Equation (26), i.e.

$$Z_i (p,T) \approx 1 + B_i'(T) p$$

The combined procedure is equivalent to using the truncated virial expansion for the whole gas mixture and expressing the mixture virial coefficient as a sum of component virial coefficients according to

$$B'_S = \sum x_i B'_i$$

Therefore the relevant application range is that of the truncated virial expansion of the whole gas mixture. This approximation is applicable at state conditions (pressure p, temperature T) where the density of the gas mixture is less than 50 % of its pseudo-critical density (see Reference [11]). Clause A.2 in Annex A specifies how this criterion can be applied in practice, using critical data of the mixture components.

Note that the truncated virial expansion may be applied to a whole gas mixture at state conditions where it breaks down for some individual components.

Starting from Amagat's Law, Equation (36), additional approximations, tailored for cases of practical importance can be derived. For example, if the gas mixture under consideration is composed of trace amounts of one or several analytes and a balance gas, the compression factor of the balance gas is an accurate approximation of the compression factor of the gas mixture.

If the composition of the gas mixture under consideration is given in volume fractions, the compression factor of the mixture can be calculated from the component compression factors using the appropriate summation relation from Annex B, as follows:

$$\frac{1}{Z_S} \approx \frac{f_S}{Z_S} = \sum_{i=1}^{N} \frac{\phi_i}{Z_i} \tag{38}$$

The uncertainty analysis for this calculation follows the same principles as those for calculations on a molar composition basis.

If the available information on the composition of the gas mixture under consideration involves other quantities than mole fractions or volume fractions, these may be converted into appropriate fractions using the ideal-gas approximation according to 6.5.1, which are then used to estimate the compression factor of the mixture.

In any case, the mixture compression factor may be estimated using the simple approximations according to 6.5.

NOTE   For natural gas refined procedures for calculating compression factors from composition, or from other physical property data are given in Parts 1 to 3 of ISO 12213[14] [15] [16] and in a monograph published by GERG[17].

7.2.3   Mixing factor

An estimate of the mixing factor may be required for the conversion of the contents of a single analyte according to 6.2 as well as for conversion of complete compositions according to 6.3.

Unless there are strong interactions between mixture components, as for example in azeotropic mixtures, the mixing factor of a gas mixture at state conditions well outside of the condensation region is close to unity. Therefore, in absence of any specific information, the mixing factor f_S is taken as unity. The uncertainty associated with this approximation is estimated as follows:

$$u^2\left(f_S = 1\right) = \frac{1}{2} \frac{\displaystyle\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i^2 x_j^2 \left(Z_i - Z_j\right)^2}{\left(\displaystyle\sum_{k=1}^{N} x_k Z_k\right)^2} \tag{39}$$

NOTE   This uncertainty estimate is based on the observation that in the vast majority of cases the interaction virial coefficient B'_{ij} for two gases i and j takes a value between those of the virial coefficients B'_i and B'_j (see Reference [19]).

If the available information on the composition of the gas mixture under consideration involves other quantities than mole fractions, these may be converted into mole fractions using the ideal-gas approximation according to 6.5.1, which are then used for an uncertainty estimation according to Equation (39).

For mixtures of non-polar gases at standard reference conditions, the standard uncertainty according to Equation (39) is of the order of magnitude 10^{-3}.

7.3   Rough uncertainty estimates

For component and mixture data determined according to the methods specified in 7.1 and 7.2, the overall standard uncertainty can be estimated roughly as follows.

— For component data:

$$u(M_i) \approx 0 \tag{40}$$

$$u(Z_i) \approx \frac{|1 - Z_i|}{\sqrt{3}} \tag{41}$$

— For mixture data:

$$u(M_S) \approx \sqrt{\sum_{k=1}^{N-1} (M_k - M_N)^2 u^2(x_k)} \tag{42}$$

$$u(Z_S) \approx \frac{|1 - Z_S|}{\sqrt{3}} \tag{43}$$

$$u(f_S) \approx 0 \tag{44}$$

In Equation (42), the Nth component is the balance gas, whose amount in the mixture is determined by difference. Equations (41) and (43) are not applicable if, on the basis of the ideal-gas approximation, compression factors are estimated to be equal to unity.

Improved uncertainty estimates for component and mixture data, and for conversion factors derived from these data, are obtained by detailed calculations of uncertainty, as specified in 7.1, 7.2 and 8.

8   Conversion uncertainty

8.1   General considerations

For most practical applications, calculations of conversion uncertainty carried out in accordance with the procedures described in this subclause require machine computation. The mathematical expressions which arise can appear complex, but are quite straightforward to perform within a well-designed computer programme. One such programme, which is available for this purpose, is described in Annex E. The user of this International Standard would be well advised not to attempt hand-calculation except for

a)   the simplest cases, and

b)   programme validation.

8.2 Conversion of single analyte contents

Conversion of single analyte contents between different quantities of composition is performed by multiplication with a conversion factor according to the schematic equation

$$O = \Omega \times I \tag{45}$$

where

I is the input (given) quantity;

O is the output (wanted) quantity;

Ω is the conversion factor.

Provided that the value of the conversion factor has been determined independently from that of the input quantity, the standard uncertainty on the output quantity is given by

$$\left[\frac{u(O)}{O}\right]^2 = \left[\frac{u(\Omega)}{\Omega}\right]^2 + \left[\frac{u(I)}{I}\right]^2 \tag{46}$$

Using relative standard uncertainties, $v(x) = u(x)/|x|$, the last equation is simplified to

$$v^2(O) = v^2(\Omega) + v^2(I) \tag{47}$$

In general, the conversion factor is a product or a quotient involving quantities of the component under consideration, quantities of the mixture under consideration, and the quantity $\alpha = p/RT$ characterizing the state conditions under consideration. Schematically

$$\Omega = \frac{K \times L \times \ldots}{P \times Q \times \ldots} \tag{48}$$

Due to this structure of Ω, the relative standard uncertainty of the conversion factor is given by

$$v^2(\Omega) = v^2(K) + v^2(L) + \ldots + v^2(P) + v^2(Q) + \ldots \tag{49}$$

This equation is based on the assumption that the values of the constituents K, L, ..., P, Q, ... have been determined independently. Otherwise, correlations have to be considered and incorporated if significant. In the same manner, if the value of the conversion factor has been estimated using the value of the input quantity, this correlation has to be considered, and incorporated, if significant.

In all uncertainty calculations, it will be assumed that the state conditions (pressure p, temperature T) under consideration are specified without uncertainty. In addition, the uncertainty of the molar gas constant, R, will be neglected.

NOTE   For conversions involving inaccurately specified state conditions, the uncertainty calculations would have to be amended correspondingly. These amendments would not only include additional terms $v^2(p)$, $v^2(T)$ or similar, but also covariance terms, resulting from correlation of errors in state conditions with errors in state-dependent quantities involved and from correlation of errors between state-dependent quantities.

As an example, consider the conversion equation of mass concentration into mole fraction as follows:

$$x_i = \frac{Z_S}{\alpha M_i} \beta_i \tag{50}$$

Assuming that the state conditions under consideration are specified without uncertainty, and neglecting the uncertainty of the molar gas constant R, the relative standard uncertainty, $v(x_i)$, of the mole fraction x_i is calculated according to

$$v^2(x_i) = v^2(Z_S) + v^2(M_i) + v^2(\beta_i) \tag{51}$$

This uncertainty calculation is based on the assumption that the quantities Z_S, M_i and β_i were determined independently, or that correlations occurring are not significant. This is not true, if the mixture compression factor was calculated from composition, and if its value is strongly dependent on the concentration of the analyte under consideration.

Since the molar masses of pure gases are very accurately known (see 7.1.1), the uncertainty $v(M_i)$ will usually be negligible. Then the uncertainty for the conversion of mass concentration into mole fraction is simply given by

$$v^2(x_i) = v^2(Z_S) + v^2(\beta_i) \tag{52}$$

Other conversions may be treated analogously, provided that they use exclusively available mixture data, which were determined independently.

If mixture data required for calculation of conversion factors are not available, these data may be estimated from pure gas data and composition data using the methods specified in 7.2. Consequently, the resulting conversion factors are dependent, among others, on the content of the component under consideration. This implies a correlation between errors in the conversion factor Ω and in the input quantity I that has to be included in the calculation of uncertainty.

Schematically, if Ω depends on I, the calculation of uncertainty for Equation (45) is given by

$$v^2(O) = v^2(\Omega) + v^2(I) + 2\frac{I}{\Omega}\frac{\partial\Omega}{\partial I}v^2(I) \tag{53}$$

In this equation, the correlation term can be neglected with respect to the term $v^2(I)$, if

$$\left|\frac{I}{\Omega}\frac{\partial\Omega}{\partial I}\right| \leqslant 0{,}1 \tag{54}$$

If Ω contains a single average, either in the numerator or in the denominator, this condition means that the component under consideration contributes at most by 10 % to the mixture property concerned.

If the condition according to Equation (54) is fulfilled, Equations (46) and (47) remain valid. For example, in the case considered above, the calculation of uncertainty according to Equations (51) and (52) is also applicable if the mixture compression factor was estimated from composition, provided that the contribution due to the component under consideration does not exceed 10 %.

Otherwise, uncertainty propagation on the basic input data, i.e. mixture composition data and component property data, has to be used (see 8.3).

8.3 Conversion of complete compositions

Conversion of complete compositions is performed using the appropriate conversion factor taken from Table 2. According to this procedure, the input fraction under consideration (e.g. w_i) is multiplied by a factor consisting of mixture composition data expressed in the same fractions (w_k) and component property data (M_k and/or Z_k). In addition, the quotient $\alpha = p/(RT)$ and the mixing factor f_S can occur.

As an example, mass fractions can be converted into mole fractions according to

$$x_i = \frac{w_i / M_i}{\sum\limits_{k} w_k / M_k}$$ (55)

The general structure of the conversion equations obtained in this manner is as follows:

$$O_i = F_i \left(I_1, I_2, ..., I_N, M_1, M_2, ..., M_N, Z_1, Z_2, ..., Z_N, f_S, \alpha \right)$$ (56)

where

O_i is the content of component i expressed in terms of the output quantity;

F_i is the mathematical function expressing the conversion for component i;

I_i is the content of component i expressed in terms of the input quantity;

I_k $(k \neq i)$ is the content of component k expressed in terms of the input quantity;

M_i (M_k) is the molar mass of component i (k);

Z_i (Z_k) is the compression factor of component i (k);

f_S is the mixing factor of the gas mixture S;

α is the quotient $p/(RT)$.

The standard uncertainty for a single output quantity O_i determined according to Equation (56) is given by combination of the uncertainties associated with the input quantities as follows:

$$
\begin{aligned}
u^2\left(O_i\right) = {} & \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial Z_k}\right)^2 u^2\left(Z_k\right) + \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial M_k}\right)^2 u^2\left(M_k\right) + \left(\frac{\partial F_i}{\partial f_S}\right)^2 u^2\left(f_S\right) \\
& + \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial I_k}\right)^2 u^2\left(I_k\right) + 2\sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\left(\frac{\partial F_i}{\partial I_k}\right)\left(\frac{\partial F_i}{\partial I_l}\right) u\left(I_k, I_l\right)
\end{aligned}
$$ (57)

where, with P and Q representing any of the quantities occurring on the right-hand side of Equation (56),

$u(P)$ is the standard uncertainty of the quantity P;

$u^2(P)$ is the variance of the quantity P (squared standard uncertainty);

$u(P,Q)$ is the covariance of the quantities P and Q;

$\partial F_i / \partial P$ is the partial derivative with respect to the quantity P.

In the calculation of uncertainty according to Equation (57), the uncertainty $u(\alpha)$ has been considered negligible. The mixing factor f_S, if relevant, will normally be considered to be equal to unity. Then $u(f_S)$ is the uncertainty associated with this estimate (see 7.2.3).

The last sum in Equation (57) takes into account that complete compositions are always significantly correlated, due to the fact that the contents of the mixture components, expressed in fractions, by definition add up to unity.

In cases where the gas mixture contains a balance component, N, whose content is determined by difference, while the contents of the other components are determined independently, explicit use of correlations can be avoided by elimination of the content of the balance gas. However this approach is generally not applicable and has computational disadvantages. Therefore, in this International Standard correlation among composition data is fully addressed. Procedures for determining the variances and covariances of input composition data are specified in 8.5.

The calculations of uncertainty for conversion of complete compositions, as given by Equation (57), are conveniently performed using numerical differentiation in a spreadsheet implementation, as outlined in 8.4.

Stand-alone calculations of uncertainty for single conversion results O_i are perfectly sufficient as long as the quantities O_i are used strictly individually. However, if several of these are used in the same application, their mutual correlation has to be taken into account. This correlation is quantified by the covariances $u(O_i, O_j)$ which are calculated from the input data variances and covariances as follows.

$$u\left(O_i, O_j\right) = \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial Z_k}\right)\left(\frac{\partial F_j}{\partial Z_k}\right) u^2\left(Z_k\right) + \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial M_k}\right)\left(\frac{\partial F_j}{\partial M_k}\right) u^2\left(M_k\right) + \left(\frac{\partial F_i}{\partial f_S}\right)\left(\frac{\partial F_k}{\partial f_S}\right) u^2\left(f_S\right)$$

$$+ \sum_{k=1}^{N}\left(\frac{\partial F_i}{\partial I_k}\right)\left(\frac{\partial F_j}{\partial I_k}\right) u^2\left(I_k\right) + \sum_{k=1}^{N-l}\sum_{l=k+1}^{N}\left[\left(\frac{\partial F_i}{\partial I_k}\right)\left(\frac{\partial F_j}{\partial I_l}\right) + \left(\frac{\partial F_i}{\partial I_l}\right)\left(\frac{\partial F_j}{\partial I_k}\right)\right] u\left(I_k, I_l\right) \tag{58}$$

In this equation, the symbols are the same as those in Equation (57).

Calculation of output data covariances for conversion of complete compositions, as given by Equation (58), is conveniently performed using numerical differentiation in a spreadsheet implementation, as outlined in 8.4.

8.4 Uncertainty calculation using numerical differentiation

Schematically, the calculation of uncertainty for a quantity Y, specified as a function of several input quantities P, Q, ... takes the form

$$u^2\left(Y\right) = \left(\frac{\partial Y}{\partial P}\right)^2 u^2\left(P\right) + \left(\frac{\partial Y}{\partial Q}\right)^2 u^2\left(Q\right) + \ldots + 2\left(\frac{\partial Y}{\partial P}\right)\left(\frac{\partial Y}{\partial Q}\right) u\left(P, Q\right) + \ldots \tag{59}$$

In this equation, the products $(\partial Y/\partial P)u(P)$, $(\partial Y/\partial Q)u(Q)$, etc., consisting of a derivative and the standard uncertainty of the input quantity concerned, can be approximated by finite differences as follows:

$$\left(\frac{\partial Y}{\partial P}\right) u\left(P\right) \approx Y\left[P + u\left(P\right)/2\right] - Y\left[P - u\left(P\right)/2\right] \tag{60}$$

If in Equation (59) correlation terms are absent or insignificant, the standard uncertainty $u(Y)$ is obtained by calculating these differences, one for each input quantity, and taking the root of the sum of squares. This computation can be conveniently performed using a spreadsheet programme (see References [4] and [5]).

If correlations are included, the same technique is applicable. Then input covariances $u(P,Q)$ are expressed as a product of the standard uncertainties $u(P)$, $u(Q)$ and the correlation coefficient $r(P,Q)$.

$$u\left(P, Q\right) = r\left(P, Q\right) u\left(P\right) u\left(Q\right) \tag{61}$$

With this presentation of the covariances, a correlation term is expressed as follows:

$$\left(\frac{\partial Y}{\partial P}\right)\left(\frac{\partial Y}{\partial Q}\right) u\left(P, Q\right) = \left[\left(\frac{\partial Y}{\partial P}\right) u\left(P\right)\right]\left[\left(\frac{\partial Y}{\partial Q}\right) u\left(Q\right)\right] r\left(P, Q\right) \tag{62}$$

Using the finite-difference approximation according to Equation (60), correlation terms are calculated from products of differences and correlation coefficients. Inclusion of correlation terms can be easily implemented in the spreadsheet technique.

The finite-difference approximation is equally applicable for the calculation of output covariances, as given by Equation (63).

$$u(Y,Y') = \left(\frac{\partial Y}{\partial P}\right)\left(\frac{\partial Y'}{\partial P}\right)u^2(P) + \left(\frac{\partial Y}{\partial Q}\right)\left(\frac{\partial Y'}{\partial Q}\right)u^2(Q) + \ldots + \left[\left(\frac{\partial Y}{\partial P}\right)\left(\frac{\partial Y'}{\partial Q}\right) + \left(\frac{\partial Y}{\partial Q}\right)\left(\frac{\partial Y'}{\partial P}\right)\right]u(P,Q) + \ldots \tag{63}$$

All the terms occurring in Equation (63) can be calculated from products of differences on the output quantities and the input correlation coefficients.

8.5 Variances and covariances of input composition data

8.5.1 General procedure

The variances and covariances of input composition data are obtained from the uncertainty analysis for the procedure by which the input composition was determined. In the case of an analysed mixture, this is an analytical procedure or a combination of different analytical procedures. In the case of synthetic mixtures, this is the preparation procedure, but often this is combined with analytical procedures for verification analysis.

For a specified analyte content, the variance is obtained by combination of the variances associated with the relevant parameters determining the result of mixture analysis, or mixture preparation, respectively. In the case of correlations between relevant parameters, covariances have to be included in the calculation of the uncertainty. The general format of these calculations is the same as that of Equation (57). Most often, however, such correlations can be avoided by going back to the basic input variables of the analytical procedure or the preparation procedure.

Covariances for the contents of different analytes are obtained by combination of the variances associated with any relevant parameters in common and the covariances between any of these. The general format of these calculations is the same as that of Equation (58). But even if the determination of different analytes is performed independently, i.e. without significant errors in common, completion and normalization of composition data give rise to significant correlations. Covariances associated with these correlations are calculated according to 8.5.2.

8.5.2 Correlation effects in complete composition data

8.5.2.1 General

By definition, in any gas mixture the mole fractions of all mixture components sum to unity. This is also true for mass fractions and volume fractions. In gas analysis, this fact is used to for two different purposes:

a) for completing mixture composition data when the fraction of the balance gas was not determined;

b) for correcting raw composition data by means of a normalization factor.

In both cases, the result is a composition data set where the fractions of the specified components sum to unity. This implies significant correlations between errors of component fractions which have to be accounted for in the calculation of uncertainty.

8.5.2.2 Balance-gas fraction by difference

Most often in complete mixture analysis, the fraction of the balance gas is not determined directly. Instead, it is calculated by difference from 1, i.e. by summing the fractions of the other components and subtracting this sum from 1.

Consider a gas mixture with components 1, 2, ..., N where N is the balance gas. Let the other analytes be determined independently, in terms of mole fractions x_1, x_2, ..., x_{N-1}, with uncertainties $u(x_1)$, $u(x_2)$, ..., $u(x_{N-1})$ and no covariances between any x_i. Then the mole fraction of the balance gas and its uncertainty are given by

$$x_N = 1 - \sum_{i=1}^{N-1} x_i \tag{64}$$

$$u^2(x_N) = \sum_{i=1}^{N-1} u^2(x_i) \tag{65}$$

Errors in mole fractions x_1, x_2, ..., x_{N-1} in Equation (64), while completely independent, cause errors in the mole fraction x_N. Due to this correlation of errors, there is a covariance between the balance gas and any of the other components as follows:

$$u(x_i, x_N) = u(x_N, x_i) = -u^2(x_i) \tag{66}$$

These covariances have to be included in the calculation of uncertainty for any conversion of the composition x_1, x_2, ..., x_N.

8.5.2.3 Normalization using a factor

In natural gas analysis, the content of the main component (methane) is often determined directly. The standard procedure is to normalize the raw mole fractions, x'_1, x'_2, ..., x'_N, by application of a normalization factor $1/\Sigma\, x'_k$ as follows:

$$x_i = \frac{x'_i}{\sum_{k=1}^{N} x'_k} \tag{67}$$

Let the raw mole fractions x'_1, x'_2, ..., x'_N, be determined completely independently, with uncertainties $u(x'_1)$, $u(x'_2)$, ..., $u(x'_N)$ and no covariances between any x'_i. An error in any raw mole fraction in Equation (67) will cause an error in the normalization factor and through this an error in each of the normalized fractions. Due to this correlation, there is a covariance between any two normalized mole fractions, as given by Equation (69). In addition to effecting correlations, however, normalization also changes the variances of the analyte fractions according to Equation (68).

$$u^2(x_i) = \frac{(1 - 2x_i)u^2(x'_i) + x_i^2 \sum_{k=1}^{N} u^2(x'_k)}{\left(\sum_{k=1}^{N} x'_k\right)^2} \tag{68}$$

$$u(x_i, x_j) = \frac{-x_i u^2(x'_j) - x_j u^2(x'_i) + x_i x_j \sum_{k=1}^{N} u^2(x'_k)}{\left(\sum_{k=1}^{N} x'_k\right)^2} \tag{69}$$

Both the changed variances and the additional covariances have to be included in the calculation of uncertainty for any conversion of the composition x_1, x_2, ..., x_N.

9 Application recommendations

Gas mixture composition should normally be specified in mole fractions, unless there are specific reasons to use other quantities of composition. The use of mole fractions is recommended because these quantities are strictly independent of state conditions, and in contrast to mass fractions, provide a good approximation to volume fractions, which are relevant in many applications.

The level of conversion uncertainty should be targeted to match the uncertainty on the input composition under consideration. It would, for example, be a waste of effort to estimate a conversion factor with an uncertainty of 0,1 % relative, using elaborate calculation methods, if the input quantity to be converted has an uncertainty of 10 %.

For the main conversion calculation between different quantities of composition for a single or specified analyte content, use the relevant conversion factor from Table 1. Select the most relevant approximation scheme for the mixture under consideration from those given in 6.5.1 to 6.5.3, then derive values (and associated uncertainties) of any physical properties of the analyte and the mixture required as input for the conversion factor using the procedures given in Clause 7. For the estimation of conversion uncertainty, use the methods described in Clause 8.

In a few rare instances, none of the approximations given in 6.5.1 to 6.5.3 might be considered appropriate for a particular gas mixture. Nevertheless, appropriate input data for Table 1 can still be calculated using the procedures given in Clause 7.

For the main conversion calculation between different quantities of composition for a complete composition, use the relevant conversion factor from Table 2. Calculate compression factors (and associated uncertainties) of mixture components required as input for the conversion factor using the procedure given in 7.1.2. If also required, estimate the mixing factor (including uncertainty) according to 7.2.3. For the estimation of conversion uncertainty, use the methods described in Clause 8.

For conversion to reference conditions, if necessary, use Equations (20) to (23), with the data required as input being derived from the same considerations as used in 8.5.2.2 or 8.5.2.3 above.

Annex A
(normative)

Assessment of state conditions

A.1 Use of saturation vapour pressure data to assess potential condensation

A.1.1 General

This clause specifies methods for assessing specified state conditions (pressure, temperature) with respect to potential condensation of gas mixtures and their components, mainly using saturation vapour pressure data.

A.1.2 Pure gases

At pressure p and temperature T a pure substance is completely gaseous if the pressure p is below the saturation vapour pressure $p_{vap}(T)$ of the substance at temperature T.

Since saturation vapour pressure increases monotonically with increasing temperature, this criterion may be extended as follows. At pressure p and temperature T, a pure substance is completely gaseous if the pressure p is below the saturation vapour pressure $p_{vap}(T')$ of the substance at any temperature $T' \leqslant T$.

Saturation vapour pressure data of pure gases are available from compilations of physico-chemical properties of pure substances, see for example References [11] and [12]. Additional references are given in Reference [10] (see in particular references C.16 to C.21 in Reference [10]).

A.1.3 Gas mixtures

At pressure p and temperature T, a mixture S is completely gaseous if the pressure p is below the dew pressure $p_{dew,S}(T)$ of S at temperature T.

As in A.1.2, this criterion may be extended as follows. At pressure p and temperature T, a mixture S is completely gaseous if the pressure p is below the dew pressure $p_{dew,S}(T')$ of S at any temperature $T' \leqslant T$.

If measured data are not available, the dew pressure of mixtures may be estimated from molar composition and the saturation vapour pressure of mixture components as follows:

$$\frac{1}{p_{dew,S}(T)} = \sum_{i=1}^{N} \frac{x_i}{p_{vap,i}(T)} \tag{A.1}$$

where

$\quad p_{dew,S}(T)$ is the dew pressure of mixture S at temperature T;

$\quad p_{vap,i}(T)$ is the saturation vapour pressure of component i at temperature T.

Using Equation (A.1), state conditions may be assessed with respect to potential mixture condensation as follows. At pressure p and temperature T, a mixture S is completely gaseous if

$$p\sum_{i=1}^{N} \frac{x_i}{p_{vap,i}(T)} < 1 \tag{A.2}$$

In this calculation, permanent gases such as nitrogen and oxygen can be disregarded (i.e. their saturation vapour pressure can considered as infinitely large). Saturation vapour pressure data of pure gases are available from compilations of physico-chemical properties of pure substances, see A.1.2.

The test according to Equation (A.2) is known to give conservative results. If the criterion is fulfilled, then it can be taken for granted that the mixture under consideration is completely gaseous at the specified state conditions. However, it may happen that the criterion is not fulfilled, while the gas mixture is in fact completely gaseous. If there are reasons to suspect a false-negative test result, the simple dew pressure estimation using Equation (A.1) may be replaced by more sophisticated calculations, based on mixture equations of state (see Reference [11]).

A.2 Use of critical data for assessing the applicability of the truncated virial expansion

A.2.1 General

This clause specifies methods, mainly using critical data, for assessing the applicability of the truncated virial expansion of the compression factor of pure gases and gas mixtures:

$$Z(p,T) = 1 + B'(T) p \tag{A.3}$$

A.2.2 Pure gases

For a pure gas, Equation (A.3) is applicable at state conditions (p,T) where the density is less than 50 % of the critical density (see Reference [11]).

Critical density data of pure gases are available from compilations of physico-chemical properties of pure substances (see A.1.2).

A.2.3 Gas mixtures

For a gas mixture, Equation (A.3) is applicable at state conditions (p,T) where the density is less than 50 % of the pseudo-critical density (see Reference [11]). For practical purposes, the pseudo-critical mixture density may be estimated from molar composition and critical data of mixture components, using "mixing rules" similar to those used for estimation of mixture compression factors (see 7.2.2).

As a simple approximation, the mixing rules according to Kay[11] may be used.

$$T_{\text{pscrit},S} = \sum_{i=1}^{N} x_i T_{\text{crit},i} \tag{A.4}$$

$$p_{\text{pscrit},S} = \sum_{i=1}^{N} x_i p_{\text{crit},i} \tag{A.5}$$

where

$T_{\text{pscrit},S}$ is the pseudo-critical temperature of mixture S;

$p_{\text{pscrit},S}$ is the pseudo-critical pressure of mixture S;

$T_{\text{crit},i}$ is the critical temperature of component i;

$p_{\text{crit},i}$ is the critical pressure of component i;

Based on these approximations, specified state conditions are assessed with respect to applicability of the truncated virial expansion as follows. Equation (A.3) is applicable at state conditions (p,T) where

$$\frac{\sum\limits_{i=1}^{N} x_i\, p_{\text{crit},i}\,/\,p}{\sum\limits_{i=1}^{N} x_i\, T_{\text{crit},i}\,/\,T} > 2 \tag{A.6}$$

Criterion (A.6) may be refined by using the mixing rule given by Prausnitz and Gunn[11] for the pseudo-critical pressure instead of using Equation (A.5).

$$p_{\text{pscrit},S} = RT_{\text{pscrit},S}\, \frac{\sum\limits_{i=1}^{N} x_i Z_{\text{crit},i}}{\sum\limits_{i=1}^{N} x_i V_{\text{crit},i}} \tag{A.7}$$

where

$p_{\text{pscrit},S}$ is the pseudo-critical pressure of mixture S;

$T_{\text{pscrit},S}$ is the pseudo-critical temperature of mixture S;

$Z_{\text{crit},i}$ is the critical compression factor of component i;

$V_{\text{crit},i}$ is the critical volume of component i.

Critical data of pure gases, as required for these calculations, are available from compilations of physico-chemical properties of pure substances (see A.1.2).

Annex B
(normative)

Summation relations for the expression of mixture properties

Table B.1 presents the basic summation relations by which the conversion factors in Table 2 are derived from the original conversion factors specified in Table 1.

Table B.1 — Basic summation relations

$$M_S = \sum x_k M_k$$

$$\frac{1}{M_S} = \sum \frac{w_k}{M_k}$$

$$\frac{Z_S}{f_S} = \sum x_k Z_k$$

$$\frac{f_S}{Z_S} = \sum \frac{\phi_k}{Z_k}$$

$$\frac{f_S M_S}{Z_S} = \sum \frac{\phi_k M_k}{Z_k}$$

$$\frac{Z_S}{f_S M_S} = \sum \frac{w_k Z_k}{M_k}$$

x_k	is the mole fraction of component k
ϕ_k	is the volume fraction of component k
w_k	is the mass fraction of component k
M_k	is the molar mass of component k
Z_k	is the compression factor of component k
M_S	is the molar mass of gas mixture S
Z_S	is the compression factor of gas mixture S
f_S	is the mixing factor of gas mixture S

All quantities refer to the specified state conditions (pressure p, temperature T) of the gas mixture under consideration.

Annex C
(informative)

Mixture component data

Table C.1 presents a compilation of data for 138 gases and liquids occurring as components of gas mixtures:

— M is the molar mass, expressed in grams per mole (g/mol);

— $u(M)$ is the standard uncertainty of the molar mass M, expressed in grams per mole (g/mol);

— B'_0 is the second pressure virial coefficient at 0 °C, expressed in 10^{-5}/kPa;

— B'_{30} is the second pressure virial coefficient at 30 °C, expressed in 10^{-5}/kPa;

— $u(B'_{dat})$ is the average standard uncertainty of the virial coefficient data B'_0, B'_{30}, expressed in 10^{-5}/kPa;

— Z_{amb} is the compression factor at 100 kPa and 15 °C (ambient conditions).

The molar masses were calculated from the IUPAC data of atomic weights of the elements (Reference [6]) according to 7.1.1. The uncertainty of the molar masses was calculated from the uncertainty of the IUPAC data of atomic weights of the elements given in Reference [7] according to 7.1.1.

Except for five gases, the virial coefficients were taken from DIN 1871 [10]. For carbon dioxide, ethane, hydrogen, methane and nitrogen, the virial coefficients were calculated from molar-volume virial coefficients taken from the GERG publication, TM2 [17]. This conversion was carried out according to the procedure used in DIN 1871. For the DIN data, the uncertainty was estimated from a detailed assessment of the input data and available information on their accuracy. For the converted GERG data, the uncertainty was estimated from the uncertainty of the original GERG data and the uncertainty associated with the conversion from molar-volume virial coefficients to pressure virial coefficients.

NOTE   In DIN 1871, the conversion from molar-volume virial coefficients $B(T)$ to pressure virial coefficients $B'(T)$ is performed differently for gases and vapours to optimize the performance of the truncated virial expansion of the compression factor [see 7.1.2, Equation (26)]. For gases (defined there as substances with normal boiling point < 0 °C, this conversion is performed according to

$$B'(T) = \frac{B(T)}{Z(p_n, T)RT} \tag{C.1}$$

where $Z(p_n, T) = 1 + B'(T) p_n$ with p_n = 101,325 kPa, resulting in a quadratic equation for $B'(T)$. For vapours (defined as substances with normal boiling point $\geqslant 0$ °C), Equation (C.1) is used with $Z(p_n, T) = 1$.

The compression factors were calculated from the virial coefficients according to 7.1.2 for those compounds that are fully gaseous at 100 kPa and 15 °C.

The data for molar masses, virial coefficients, and their uncertainties are used in the computer programme that is available for use with this International Standard (see Annex E).

Table C.1 — Mixture component data

Component	Formula	M	$u(M)$	B'_0	B'_{30}	$u(B'_{dat})$	Z_{amb}
Acetylene	C_2H_2	26,037 3	0,001 6	− 8,4	− 5,8	0,5	0,992 90
Air	—	28,962 5	0,000 2	− 0,58	− 0,27	0,02	0,999 58
Ammonia	NH_3	17,030 6	0,000 3	− 14,9	− 9,7	0,5	0,987 70
Argon	Ar	39,948 0	0,000 1	− 0,96	− 0,61	0,05	0,999 22
Arsine	AsH_3	77,945 4	0,000 3	− 12	− 9	0,5	0,989 50
Benzene	C_6H_6	78,112 0	0,004 9	− 82	− 57	5	—
Boron trichloride	BCl_3	117,169 0	0,008 0	− 39	− 29	3	0,966 00
Boron trifluoride	BF_3	67,806 0	0,007 0	− 6	− 4	0,5	0,995 00
Bromochlorodifluoromethane	$CBrClF_2$	165,364 2	0,001 5	− 34	− 24	0,5	0,971 00
Bromomethane	CH_3Br	94,938 5	0,001 4	− 31,1	− 20,5	0,5	0,974 20
Bromotrifluoromethane	$CBrF_3$	148,909 9	0,001 4	− 17	− 13	0,5	0,985 00
1,2-Butadiene	C_4H_6	54,090 4	0,004 0	− 45	− 31	5	0,962 00
1,3-Butadiene	C_4H_6	54,090 4	0,004 0	− 34	− 24	1	0,971 00
n-Butane	C_4H_{10}	58,122 2	0,004 0	− 42,2	− 28,9	0,2	0,964 45
1-Butene	C_4H_8	56,106 3	0,003 3	− 35	− 25	1	0,970 00
cis-2-Butene	C_4H_8	56,106 3	0,003 3	− 39	− 27	2	0,967 00
trans-2-Butene	C_4H_8	56,106 3	0,003 3	− 38	− 27	2	0,967 50
1-Butyne	C_4H_6	54,090 4	0,004 0	− 43,6	− 29,9	1	0,963 25
Carbon dioxide	CO_2	44,009 5	0,001 1	− 6,69	− 4,75	0,03	0,994 28
Carbon disulfide	CS_2	76,143 0	0,013 0	− 45	− 32	1	—
Carbon monoxide	CO	28,010 1	0,000 9	− 0,66	− 0,31	0,05	0,999 52
Carbonyl chloride	$COCl_2$	98,915 5	0,002 0	− 32	− 22	3	0,973 00
Carbonyl fluoride	COF_2	66,006 9	0,000 9	− 8	− 6	0,2	0,993 00
Carbonyl sulfide	COS	60,076 0	0,006 2	− 14,9	− 10,8	0,5	0,987 15
Chlorine	Cl_2	70,905 4	0,001 8	− 15,8	− 11,8	0,1	0,986 20
Chlorine trifluoride	ClF_3	92,447 9	0,000 9	− 34	− 24	3	0,971 00
1-Chloro-1,1-difluoroethane	$C_2H_3ClF_2$	100,495 0	0,002 0	− 49,6	− 31	0,2	0,959 70
Chlorodifluoromethane	$CHClF_2$	86,468 1	0,001 2	− 19,1	− 13,7	0,1	0,983 60
Chloroethane	C_2H_5Cl	64,513 8	0,001 9	− 43	− 29	3	0,964 00
Chloromethane	CH_3Cl	50,487 2	0,001 3	− 23,1	− 15,8	0,1	0,980 55
Chloropentafluoride	ClF_5	130,444 7	0,000 9	− 27,5	− 19,3	1	0,976 60
Chloropentafluoroethane	C_2ClF_5	154,466 1	0,001 9	− 22,5	− 15,8	0,1	0,980 85

Table C.1 (*continued*)

Component	Formula	M	$u(M)$	B'_0	B'_{30}	$u(B'_{dat})$	Z_{amb}
1-Chloro-1,1,2,2-tetrafluoroethane	C_2HClF_4	136,475 7	0,001 9	− 36,5	− 25,3	1	0,969 10
Chlorotrifluoroethene	C_2ClF_3	116,469 3	0,001 9	− 26	− 18	0,2	0,978 00
Chlorotrifluoromethane	$CClF_3$	104,458 6	0,001 2	− 12,1	− 8,6	0,1	0,989 65
Cyanogen	C_2N_2	52,035 0	0,001 7	− 24	− 15	0,5	0,980 50
Cyanogen chloride	$CClN$	61,470 1	0,001 2	− 35	− 23	3	0,971 00
Cyclobutane	C_4H_8	56,106 3	0,003 3	− 36,2	− 25,3	0,5	0,969 25
Cyclohexane	C_6H_{12}	84,160 0	0,004 9	− 101	− 66	5	—
Cyclopentane	C_5H_{10}	70,133 0	0,004 1	− 64	− 43	3	—
Cyclopropane	C_3H_6	42,079 7	0,002 5	− 21,1	− 15,0	0,1	0,981 95
n-Decane	$C_{10}H_{22}$	142,282 0	0,009 0	− 558	− 312	10	—
Deuterium	D_2	4,028 0	0,000 3	0,58	0,56	0,05	1,000 57
Diborane	B_2H_6	27,670 0	0,015 0	− 10	− 7	0,5	0,991 50
Dichlorodifluoromethane	CCl_2F_2	120,913 0	0,002 0	− 27,5	− 18,3	0,2	0,977 10
Dichlorofluoromethane	$CHCl_2F$	102,922 4	0,002 0	− 31,1	− 22,1	1	0,973 40
Dichlorosilane	SiH_2Cl_2	101,006 8	0,001 9	− 34	− 25	3	0,970 50
1,2-Dichlorotetrafluoroethane	$C_2Cl_2F_4$	170,920 4	0,002 4	− 39,9	− 27,5	1	0,966 30
1,1-Difluoroethane	$C_2H_4F_2$	66,050 0	0,001 7	− 30,6	− 20,0	0,2	0,974 70
1,1-Difluoroethene	$C_2H_2F_2$	64,034 1	0,001 7	− 10,4	− 7,4	0,5	0,991 10
2,2-Dimethylbutane	C_6H_{14}	86,175 0	0,005 0	− 82,9	− 56,6	1	—
2,3-Dimethylbutane	C_6H_{14}	86,175 0	0,005 0	− 81	− 59	5	—
Dimethyl ether	C_2H_6O	46,068 4	0,001 7	− 27	− 19	0,5	0,977 00
Dimethylamine	C_2H_7N	45,083 7	0,001 7	− 38,3	− 25,8	0,5	0,967 95
Disilane	Si_2H_6	62,218 6	0,000 8	− 26	− 19	0,5	0,977 50
Ethane	C_2H_6	30,069 0	0,001 7	− 9,86	− 7,16	0,05	0,991 49
Ethene	C_2H_4	28,053 2	0,001 7	− 7,43	− 5,39	0,05	0,993 59
Ethyl methyl ether	C_3H_8O	60,095 0	0,002 5	− 33,7	− 22,8	1	0,971 75
Ethylamine	C_2H_7N	45,083 7	0,001 7	− 45,1	− 29,9	0,5	—
Ethylbenzene	C_8H_{10}	106,165 0	0,006 5	− 233	− 137	10	—
Ethylcyclohexane	C_8H_{16}	112,213 0	0,006 6	− 227	− 138	10	—
Ethylcyclopentane	C_7H_{14}	98,186 0	0,005 8	− 157	− 98	10	—
Ethylene oxide	C_2H_4O	44,052 6	0,001 7	− 32	− 23	3	0,972 50
Fluorine	F_2	37,996 8	0,000 0	− 0,66	− 0,37	0,02	0,999 49

Table C.1 (*continued*)

Component	Formula	M	$u(M)$	B'_0	B'_{30}	$u(B'_{dat})$	Z_{amb}
Fluoroethane	C_2H_5F	48,059 5	0,001 7	− 19	− 14	0,5	0,983 50
Fluoromethane	CH_3F	34,032 9	0,000 9	− 11,7	− 8,0	0,2	0,990 15
Germane	GeH_4	76,642 0	0,021 0	− 9,1	− 6,6	1	0,992 15
Helium	He	4,002 6	0,000 0	0,53	0,47	0,05	1,000 50
1-H-Heptafluoropropane	C_3HF_7	170,029 0	0,002 5	− 42	− 29	0,5	0,964 50
n-Heptane	C_7H_{16}	100,202 0	0,005 8	− 168	− 106	10	—
n-Hexane	C_6H_{14}	86,176 0	0,005 0	− 106	− 70	5	—
Hexafluoroethane	C_2F_6	138,011 8	0,001 7	− 14,2	− 9,94	0,02	0,987 93
Hexafluoropropene	C_3F_6	150,023 0	0,002 5	− 31	− 23	1	0,973 00
Hydrogen	H_2	2,015 9	0,000 2	0,605	0,574	0,001	1,000 59
Hydrogen bromide	HBr	80,911 9	0,001 1	− 9,6	− 7,0	1	0,991 70
Hydrogen chloride	HCl	36,460 6	0,000 9	− 9,3	− 6,4	0,1	0,992 15
Hydrogen cyanide	HCN	27,025 4	0,000 9	− 111	− 64	5	—
Hydrogen fluoride	HF	20,006 3	0,000 1	− 35,6	− 24,1	3	—
Hydrogen iodide	HI	127,912 4	0,000 1	− 15,1	− 11,1	1	0,986 90
Hydrogen selenide	H_2Se	80,976 0	0,030 0	− 12,9	− 9,5	1	0,988 80
Hydrogen sulfide	H_2S	34,082 0	0,006 1	− 10	− 7	0,5	0,991 50
Isobutane	C_4H_{10}	58,122 2	0,003 3	− 37,9	− 27,1	1	0,967 50
Isobutene	C_4H_8	56,106 3	0,003 3	− 35	− 25	1	0,970 00
Isopentane	C_5H_{12}	72,149 0	0,004 2	− 58	− 42	5	—
Krypton	Kr	83,800 0	0,010 0	− 2,74	− 1,95	0,02	0,997 66
Methane	CH_4	16,042 5	0,000 9	− 2,36	− 1,63	0,005	0,998 01
Methanol	CH_4O	32,041 9	0,001 0	− 173	− 73	5	—
Methylamine	CH_5N	31,057 1	0,000 9	− 30,7	− 19,8	0,1	0,974 75
Methylcyclohexane	C_7H_{14}	98,186 0	0,005 8	− 143,3	− 91,1	1	—
Methylcyclopentane	C_6H_{12}	84,160 0	0,004 9	− 96,8	− 63,7	1	—
Methyl mercaptan	CH_4S	48,108 0	0,006 2	− 27,4	− 19,3	1	0,976 65
2-Methylpentane	C_6H_{14}	86,175 0	0,005 0	− 90,4	− 65,1	1	—
3-Methylpentane	C_6H_{14}	86,175 0	0,005 0	− 90,3	− 64,3	1	—
Methyl vinyl ether	C_3H_6O	58,079 0	0,002 5	− 34	− 24	3	0,971 00
Neon	Ne	20,179 7	0,000 6	0,47	0,46	0,02	1,000 47
Neopentane	C_5H_{12}	72,149 0	0,004 2	− 53,1	− 35,4	1	0,955 75
Nitric oxide	NO	30,006 1	0,000 4	− 1,12	− 0,75	0,05	0,999 07
Nitrogen	N_2	28,013 5	0,000 2	− 0,452	− 0,151	0,001	0,999 70

Table C.1 (*continued*)

Component	Formula	M	$u(M)$	B'_0	B'_{30}	$u(B'_{dat})$	Z_{amb}
Nitrogen dioxide	NO_2	46,005 5	0,000 7	− 26,4	− 17,0	2	—
Nitrogen trifluoride	NF_3	71,001 9	0,000 1	− 5	− 3	0,5	0,996 00
Nitrosyl chloride	$NOCl$	65,458 8	0,001 0	− 21	− 14	0,5	0,982 50
Nitrous oxide	N_2O	44,012 9	0,000 4	− 7,18	− 5,08	0,05	0,993 87
n-Nonane	C_9H_{20}	128,255 0	0,007 4	382	− 222	10	—
n-Octane	C_8H_{18}	114,229 0	0,006 6	− 255	− 155	10	—
Octafluoro-2-butene	C_4F_8	200,030 0	0,003 3	− 54	− 37	5	0,954 50
Octafluorocyclobutane	C_4F_8	200,030 0	0,003 3	− 43,7	− 29,8	0,5	0,963 25
Octafluoropropane	C_3F_8	188,019 0	0,002 5	− 30,1	− 20,6	0,5	0,974 65
Oxygen	O_2	31,998 8	0,000 7	− 0,97	− 0,60	0,02	0,999 22
Oxygen difluoride	OF_2	53,996 2	0,000 4	− 3,3	− 2,3	0,3	0,997 20
n-Pentane	C_5H_{12}	72,149 0	0,004 2	− 74	− 48,5	1	—
1-Pentene	C_5H_{10}	70,133 0	0,004 1	− 61,1	− 42,1	0,5	—
Phosphine	PH_3	33,997 6	0,000 2	− 9,2	− 6,7	0,1	0,992 05
Phosphorus pentafluoride	PF_5	125,965 8	0,000 0	− 12,9	− 9,1	1	0,989 00
Phosphorus trifluoride	PF_3	87,969 0	0,000 0	− 8,2	− 5,5	1	0,993 15
Propadiene	C_3H_4	40,064 0	0,002 5	− 20,4	− 14,6	0,2	0,982 50
Propane	C_3H_8	44,096 0	0,002 5	− 20,87	− 14,79	0,1	0,982 17
Propene	C_3H_6	42,080 0	0,002 5	− 18,7	− 13,4	0,1	0,983 95
Propyne	C_3H_4	40,064 0	0,002 5	− 23,0	− 15,9	0,5	0,980 55
Silane	SiH_4	32,117 3	0,000 5	− 7	− 5	0,2	0,994 00
Silicon tetrafluoride	SiF_4	104,079 1	0,000 4	− 8	− 5	0,5	0,993 50
Sulfur dioxide	SO_2	64,065 0	0,006 2	− 24	− 17	2	0,979 50
Sulfur hexafluoride	SF_6	146,056 0	0,006 1	− 15,2	− 10,8	0,1	0,987 00
Sulfuryl fluoride	SO_2F_2	102,062 0	0,006 2	− 15,5	− 11,4	1	0,986 55
Tetrafluoroethene	C_2F_4	100,015 0	0,001 7	− 11,5	− 8,2	0,5	0,990 15
Tetrafluoromethane	CF_4	88,004 3	0,000 9	− 4,9	− 3,4	0,05	0,995 85
Toluene	C_7H_8	92,139 0	0,005 7	− 150	− 92,1	1	—
1,1,1-Trifluoroethane	$C_2H_3F_3$	84,040 4	0,001 7	− 19,2	− 13,5	0,2	0,983 65
Trifluoromethane	CHF_3	70,013 8	0,000 9	− 9,7	− 6,9	0,1	0,991 70
Trimethylamine	C_3H_9N	59,110 3	0,002 5	− 40,4	− 28,3	0,5	0,965 65
Tungsten hexafluoride	WF_6	297,830 4	0,010 0	− 46	− 32	3	—
Vinyl bromide	C_2H_3Br	106,949 2	0,002 0	− 35	− 26	3	—

Table C.1 (*continued*)

Component	Formula	M	$u(M)$	B'_0	B'_{30}	$u(B'_{dat})$	Z_{amb}
Vinyl chloride	C_2H_3Cl	62,497 9	0,001 9	− 22	− 16	1	0,981 00
Vinyl fluoride	C_2H_3F	46,043 6	0,001 7	− 15	− 10	0,5	0,987 50
Water	H_2O	18,015 3	0,000 4	− 80,75	− 42,61	0,1	—
Xenon	Xe	131,290 0	0,020 0	− 6,8	− 5,0	0,05	0,994 10
m-Xylene	C_8H_{10}	106,165 0	0,006 5	− 248	− 145	10	—
o-Xylene	C_8H_{10}	106,165 0	0,006 5	− 259	− 149	10	—
p-Xylene	C_8H_{10}	106,165 0	0,006 5	− 246	− 144	10	—

Annex D
(informative)

Examples

D.1 Introductory remarks

The purpose of this annex is to provide some examples for conversions of gas mixture composition to other quantities of composition or to other reference conditions. Except for some simple calculations, the conversions and uncertainty calculations were performed using the computer programme CONVERT that is available for this International Standard (see Annex E). Where appropriate, arrays of data generated by CONVERT were copied directly from the output.

Standard uncertainties can hardly be estimated with a precision better than 10 %, and for estimates of covariances and correlation coefficients precision can be even worse. Therefore these data should not be specified by more than two digits. However, for comparison purposes output of the computer programme CONVERT is given with a higher number of digits.

D.2 Conversion of a complete composition

D.2.1 Example 1 — Natural gas

D.2.1.1 General considerations

This example concerns the analysis of natural gas composition which is usually determined and reported as a set of normalized mole fractions for the quantified components, i.e. where the mole fractions of all components sum to unity. The example highlights the different procedures commonly used for this purpose, including the calculation of uncertainty. While the molar composition is fit for many practical purposes such as calculation of physical properties of natural gas, occasionally (e.g. for the calculation of flammability limits), the composition is required in volume fractions at specified reference conditions. The example addresses the conversion from mole fractions to volume fractions at different reference conditions, taking into account the presence of condensable components and including the calculation of uncertainty.

D.2.1.2 Establishing the initial molar composition and composition uncertainty

Consider a natural gas where the following components were determined quantitatively in mole fractions (while methane as the main component was not determined):

Component 1: ethane (C_2H_6)	$0,035\ 00 \pm 0,000\ 086$
Component 2: propane (C_3H_8)	$0,009\ 80 \pm 0,000\ 032$
Component 3: n-butane (C_4H_{10})	$0,002\ 20 \pm 0,000\ 010$
Component 4: isobutane (C_4H_{10})	$0,003\ 40 \pm 0,000\ 006$
Component 5: pentanes (C_5H_{12})	$0,000\ 60 \pm 0,000\ 004$
Component 6: nitrogen (N_2)	$0,017\ 50 \pm 0,000\ 064$
Component 7: carbon dioxide (CO_2)	$0,006\ 80 \pm 0,000\ 052$

In the listing, the data are given in the format *value ± standard uncertainty*. All the components were determined independently. Therefore there is no correlation (covariance) between any of them.

Assuming that residual components can be neglected, the mole fraction of methane is given by summing the mole fractions of Components 1 to 7 and subtracting this sum from unity. This gives

Component 8: methane (CH_4)   0,924 70

The standard uncertainty of the methane content is calculated as the root of the sum of squared standard uncertainties of the other components according to Equation (65) in 8.5.2. This calculation gives u(methane) = 0,000 124.

Due to the determination of methane by difference, there is a correlation between errors of the methane content and the content of any other component. Consequently, there are covariances between methane and each of the other components that have to be included in the calculation of uncertainty for the complete composition. These covariances are given by Equation (66).

Altogether, the complete variance/covariance matrix for the molar composition above is given as follows:

```
 7,396E-09   0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00  -7,396E-09
 0,000E+00   1,024E-09   0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00  -1,024E-09
 0,000E+00   0,000E+00   1,000E-10   0,000E+00   0,000E+00   0,000E+00   0,000E+00  -1,000E-10
 0,000E+00   0,000E+00   0,000E+00   3,600E-11   0,000E+00   0,000E+00   0,000E+00  -3,600E-11
 0,000E+00   0,000E+00   0,000E+00   0,000E+00   1,600E-11   0,000E+00   0,000E+00  -1,600E-11
 0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00   4,096E-09   0,000E+00  -4,096E-09
 0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00   0,000E+00   2,704E-09  -2,704E-09
-7,396E-09  -1,024E-09  -1,000E-10  -3,600E-11  -1,600E-11  -4,096E-09  -2,704E-09   1,537E-08
```

Instead of the variance/covariance matrix, the correlation matrix may be used. The elements of this matrix are the correlation coefficients, which are obtained by standardizing covariances and variances using the corresponding standard uncertainties.

$$r\left(x_i, x_k\right) = \frac{u\left(x_i, x_k\right)}{u\left(x_i\right) u\left(x_k\right)} \tag{D.1}$$

The correlation coefficients $r\left(x_i, x_k\right)$ are restricted to values between +1 and –1, where positive and negative values express positive correlation and negative correlation, respectively. For uncorrelated estimates, the correlation coefficient is zero.

The computer programme CONVERT available for this International Standard (see Annex E) allows calculation of both, the variance/covariance matrix and the correlation matrix. For the composition above, the correlation matrix is given by

```
 1,0000   0,0000   0,0000   0,0000   0,0000   0,0000   0,0000  -0,6936
 0,0000   1,0000   0,0000   0,0000   0,0000   0,0000   0,0000  -0,2581
 0,0000   0,0000   1,0000   0,0000   0,0000   0,0000   0,0000  -0,0807
 0,0000   0,0000   0,0000   1,0000   0,0000   0,0000   0,0000  -0,0484
 0,0000   0,0000   0,0000   0,0000   1,0000   0,0000   0,0000  -0,0323
 0,0000   0,0000   0,0000   0,0000   0,0000   1,0000   0,0000  -0,5162
 0,0000   0,0000   0,0000   0,0000   0,0000   0,0000   1,0000  -0,4194
-0,6936  -0,2581  -0,0807  -0,0484  -0,0323  -0,5162  -0,4194   1,0000
```

The correlations between the methane content and the content of other components are irrelevant for applications where only single analyte contents are used. However, in applications jointly addressing several analytes or the complete composition, as in the conversion to follow, correlations between mixture

components have to be included in the calculation of uncertainty. Otherwise grossly erroneous uncertainty estimates can be obtained (see D.2.2).

Assume now that the mole fraction of methane was also determined directly and independently of the other components as follows:

Component 8: methane (CH_4) 0,923 0 ± 0,001 5

Then the preferred procedure is to normalize the "raw molar composition". Normalization is performed by dividing each raw mole fraction by the sum of all raw mole fractions, as described in Equation (67) of 8.5.2.3. The standard uncertainty of the normalized mole fractions is calculated according to Equation (68). In this manner, the normalized composition including standard uncertainties is obtained as follows:

Component 1: ethane (C_2H_6) 0,035 06 ± 0,000 098

Component 2: propane (C_3H_8) 0,009 82 ± 0,000 035

Component 3: *n*-butane (C_4H_{10}) 0,002 20 ± 0,000 010

Component 4: isobutane (C_4H_{10}) 0,003 41 ± 0,000 008

Component 5: pentanes (C_5H_{12}) 0,000 60 ± 0,000 004

Component 6: nitrogen (N_2) 0,017 53 ± 0,000 068

Component 7: carbon dioxide (CO_2) 0,006 81 ± 0,000 053

Component 8: methane (CH_4) 0,924 57 ± 0,000 161

The differences between raw mole fractions and normalized mole fractions are well covered by the uncertainties of the raw mole fractions. Thus the use of the normalized mole fractions and their uncertainties is fully justified.

Due to the normalization procedure, a correlation is introduced among all the components. The corresponding covariances are calculated according to Equation (69). Instead of the variance/ covariance matrix, here the correlation matrix is given.

```
 1,0000   0,1953   0,1502   0,3152   0,1061   0,1670   0,0765  -0,7763
 0,1953   1,0000   0,1245   0,2611   0,0879   0,1392   0,0641  -0,4392
 0,1502   0,1245   1,0000   0,2002   0,0674   0,1070   0,0494  -0,2569
 0,3152   0,2611   0,2002   1,0000   0,1413   0,2247   0,1039  -0,4437
 0,1061   0,0879   0,0674   0,1413   1,0000   0,0756   0,0349  -0,1640
 0,1670   0,1392   0,1070   0,2247   0,0756   1,0000   0,0544  -0,5931
 0,0765   0,0641   0,0494   0,1039   0,0349   0,0544   1,0000  -0,4197
-0,7763  -0,4392  -0,2569  -0,4437  -0,1640  -0,5931  -0,4197   1,0000
```

Comparing the results obtained when the methane fraction is determined by difference from unity and when a complete composition is normalized, the uncertainties are similar, but normalization of a complete composition gives rise to broader correlation. The values obtained for the mole fractions of the components agree within their uncertainties.

It is not uncommon that different data evaluation procedures give different estimates. This is no problem if these estimates agree within their uncertainties. Then both estimates may be used equivalently. Otherwise a decision has to be taken, based on additional information or criteria. In this example, the normalized composition would be preferred, because it includes the information obtained by direct determination of the methane content.

D.2.1.3 Conversion to volume fractions

The two molar compositions obtained above are now converted to volume fractions at two different reference conditions as follows:

⎯ Reference conditions 1: p = 101,325 kPa, T = 298,15 K

⎯ Reference conditions 2: p = 101,325 kPa, T = 273,15 K

In the following conversion, the pentanes are taken as *n*-pentane.

Using the programme CONVERT, the volume fractions and their standard uncertainties are obtained as given in Table D.1.

Table D.1 — Results of conversion to volume fractions

| Component | Reference conditions 1 p = 101,325 kPa, T = 298,15 K | |
| | Input: completed composition (methane by difference) | Input: normalized complete composition |
	Volume fraction	Volume fraction
Ethane	$3,481\ 0 \times 10^{-2} \pm 8,56 \times 10^{-5}$	$3,487\ 0 \times 10^{-2} \pm 9,80 \times 10^{-5}$
Propane	$9,665\ 4 \times 10^{-3} \pm 3,16 \times 10^{-5}$	$9,681\ 8 \times 10^{-3} \pm 3,46 \times 10^{-5}$
n-Butane	$2,135\ 6 \times 10^{-3} \pm 9,82 \times 10^{-6}$	$2,139\ 2 \times 10^{-3} \pm 1,03 \times 10^{-5}$
Isobutane	$3,308\ 1 \times 10^{-3} \pm 7,05 \times 10^{-6}$	$3,313\ 7 \times 10^{-3} \pm 8,64 \times 10^{-6}$
Pentanes	$(5,692\ 4 \times 10^{-4} \pm 3,99 \times 10^{-6})$	$(5,702\ 1 \times 10^{-4} \pm 4,09 \times 10^{-6})$
Nitrogen	$1,753\ 7 \times 10^{-2} \pm 6,41 \times 10^{-5}$	$1,756\ 7 \times 10^{-2} \pm 6,84 \times 10^{-5}$
CO_2	$6,780\ 7 \times 10^{-3} \pm 5,19 \times 10^{-5}$	$6,792\ 2 \times 10^{-3} \pm 5,26 \times 10^{-5}$
Methane	$9,251\ 9 \times 10^{-1} \pm 1,24 \times 10^{-4}$	$9,250\ 7 \times 10^{-1} \pm 1,61 \times 10^{-4}$
Component	Reference conditions 2 p = 101,325 kPa, T = 273,15 K	
	Input: completed composition (methane by difference)	Input: normalized complete composition
	Volume fraction	Volume fraction
Ethane	$3,475\ 8 \times 10^{-2} \pm 8,55 \times 10^{-5}$	$3,481\ 7 \times 10^{-2} \pm 9,79 \times 10^{-5}$
Propane	$9,622\ 5 \times 10^{-3} \pm 3,15 \times 10^{-5}$	$9,638\ 9 \times 10^{-3} \pm 3,45 \times 10^{-5}$
n-Butane	$2,112\ 5 \times 10^{-3} \pm 9,92 \times 10^{-6}$	$2,116\ 1 \times 10^{-3} \pm 1,04 \times 10^{-5}$
Isobutane	$3,279\ 6 \times 10^{-3} \pm 7,38 \times 10^{-6}$	$3,285\ 2 \times 10^{-3} \pm 8,89 \times 10^{-6}$
Pentanes	$(5,567\ 3 \times 10^{-4} \pm 4,31 \times 10^{-6})$	$(5,576\ 8 \times 10^{-4} \pm 4,40 \times 10^{-6})$
Nitrogen	$1,754\ 6 \times 10^{-2} \pm 6,42 \times 10^{-5}$	$1,757\ 6 \times 10^{-2} \pm 6,85 \times 10^{-5}$
CO_2	$6,774\ 9 \times 10^{-3} \pm 5,18 \times 10^{-5}$	$6,786\ 4 \times 10^{-3} \pm 5,26 \times 10^{-5}$
Methane	$9,253\ 5 \times 10^{-1} \pm 1,24 \times 10^{-4}$	$9,252\ 2 \times 10^{-1} \pm 1,60 \times 10^{-4}$

In Table D.1, the volume fraction of pentanes is given in brackets, since only one of the three isomeric pentanes is gaseous at normal pressure and 25 °C, while none of them are gaseous at normal pressure and 0 °C. Therefore, volume fractions should not be used for this component. However, calculation of flammability limits requires volume fractions for all components of a gas, including volume fractions for liquids in a hypothetical gaseous state at the reference conditions under consideration.

For the converted compositions at 25 °C, the correlation matrix is obtained as follows:

Table D.2 — Correlation matrix for converted compositions

```
p = 101,325 kPa, T = 298,15 K, input: completed composition (methane by difference)
     1,0000    0,0003    0,0001   -0,0006    0,0000    0,0001    0,0001   -0,6923
     0,0003    1,0000    0,0001   -0,0005    0,0000    0,0001    0,0001   -0,2561
     0,0001    0,0001    1,0000   -0,0004    0,0000    0,0000    0,0001   -0,0796
    -0,0006   -0,0005   -0,0004    1,0000   -0,0004   -0,0006   -0,0002   -0,0560
     0,0000    0,0000    0,0000   -0,0004    1,0000   -0,0001    0,0000   -0,0322
     0,0001    0,0001    0,0000   -0,0006   -0,0001    1,0000    0,0000   -0,5186
     0,0001    0,0001    0,0001   -0,0002    0,0000    0,0000    1,0000   -0,4194
    -0,6923   -0,2561   -0,0796   -0,0560   -0,0322   -0,5186   -0,4194    1,0000

p = 101,325 kPa, T = 298,15 K, input: normalized complete composition
     1,0000    0,1951    0,1487    0,2797    0,1010    0,1671    0,0766   -0,7754
     0,1951    1,0000    0,1231    0,2313    0,0836    0,1390    0,0641   -0,4371
     0,1487    0,1231    1,0000    0,1758    0,0635    0,1060    0,0490   -0,2538
     0,2797    0,2313    0,1758    1,0000    0,1194    0,1994    0,0923   -0,4037
     0,1010    0,0836    0,0635    0,1194    1,0000    0,0720    0,0333   -0,1572
     0,1671    0,1390    0,1060    0,1994    0,0720    1,0000    0,0545   -0,5950
     0,0766    0,0641    0,0490    0,0923    0,0333    0,0545    1,0000   -0,4200
    -0,7754   -0,4371   -0,2538   -0,4037   -0,1572   -0,5950   -0,4200    1,0000
```

The correlation data for 0 °C are very close to those for 25 °C.

These correlations would have to be considered in estimating the uncertainty of flammability limits derived from a converted composition.

D.2.2 Example 2 — Gravimetric preparation

D.2.2.1 General considerations

This example refers to the gravimetric preparation of a multi-component gas mixture in a pressure cylinder. It includes calculation of an initial composition in mass fractions from the weighing results, conversion of the initial mass-based composition into a molar composition (i.e. in mole fractions), and calculation of mixture properties (density and calorific value) from the molar composition and related component properties. A simplified uncertainty analysis is given for the initial composition in mass fractions, the converted composition in mole fractions, and for the derived mixture properties.

For simplicity, the calculation of uncertainty is restricted to the following uncertainty sources:

— weighing uncertainty: cylinder weighings are assumed to be mutually independent, with a constant uncertainty;

— uncertainty of molar masses: uncertainties of component molar masses are calculated from the uncertainties of the molar masses of the elements and correlation between molar masses of compounds containing elements in common is considered negligible.

All other sources of uncertainty, in particular those associated with impurities of the parent gases, are disregarded.

As an example, a natural gas simulate consisting of carbon dioxide (CO_2), nitrogen (N_2), ethane (C_2H_6) and methane (CH_4) is used.

As far as useful, the calculations of uncertainty are presented in general terms as well as in numerical form for the specified example.

D.2.2.2   Initial mass-based composition

A mixture with components 1, 2, ..., N is prepared by transferring portions of parent gases 1, 2, ..., N one after the other from donor cylinders into a receptor cylinder. The amount of each gas transferred into the receptor cylinder is determined by weighing the receptor cylinder before and after the transfer. In the course of this process, a series of weighing results is obtained as follows:

W_0 mass of the evacuated cylinder

W_1 mass of the cylinder after transfer of Component 1

W_2 mass of the cylinder after transfer of Component 2

...

W_N mass of the cylinder after transfer of Component N

The component masses are given by the difference of successive weighings:

$$m_i = W_i - W_{i-1}$$

and the total mass of gas is given by

$$m_{\text{tot}} = \Sigma m_i = W_N - W_0$$

From these relations, the mass fractions of the components are obtained as follows:

$$w_i = \frac{m_i}{m_{\text{tot}}} = \frac{W_i - W_{i-1}}{W_N - W_0} \tag{D.2}$$

Assuming that all weighings were performed independently with a constant standard uncertainty $u(W) = u$, the variances of the component masses and the total mass are given by $u^2(m_i) = 2u^2$ and $u^2(m_{\text{tot}}) = 2u^2$. In addition, there are non-zero covariances between the masses of adjacent components according to $u(m_i, m_k) = -u^2$ for $|i - k| = 1$, and there are also non-zero covariances between the total mass and the masses of the initial and the final component in the filling sequence according to $u(m_i, m_{\text{tot}}) = u^2$ for $i = 1$ and $i = N$. From these input uncertainties, the variances and covariances of the component mass fractions are obtained as follows:

$$u\left(w_i, w_k\right) = \left(\frac{\partial w_i}{\partial m_{\text{tot}}}\right)\left(\frac{\partial w_k}{\partial m_{\text{tot}}}\right)u^2\left(m_{\text{tot}}\right) + \left(\frac{\partial w_i}{\partial m_i}\right)\left(\frac{\partial w_k}{\partial m_k}\right)u\left(m_i, m_k\right)$$

$$+ \left(\frac{\partial w_i}{\partial m_i}\right)\left(\frac{\partial w_k}{\partial m_{\text{tot}}}\right)u\left(m_i, m_{\text{tot}}\right) + \left(\frac{\partial w_i}{\partial m_{\text{tot}}}\right)\left(\frac{\partial w_k}{\partial m_k}\right)u\left(m_{\text{tot}}, m_k\right) \tag{D.3}$$

In Equation (D.3), the following convention is used to express both covariances and variances: $u(w_i, w_i) = u^2(w_i)$, $u(m_i, m_i) = u^2(m_i)$. With the results obtained previously for the variances and covariances of the component masses and the total mass, the entries of the variance/covariance matrix of the component mass fractions are obtained as follows:

$$u\left(w_i, w_k\right) = \left(\frac{u}{m_{\text{tot}}}\right)^2 \times \text{2nd-order term in } w_i, w_k \tag{D.4}$$

The factors in Equation (D.4) are given as follows:

— Factors for variances

For $i = k = 1$: $\qquad\qquad 2w_1^2 - 2w_1 + 2$

For $i = k = N$: $\qquad\qquad 2w_N^2 - 2w_N + 2$

For $1 < i = k < N$: $\qquad 2w_i^2 + 2$

— Factors for borderline covariances

For $i = 1$; $k = 2$: $\qquad\qquad 2w_1w_2 - w_2 - 1$

For $i = 1$; $2 < k < N$: $\qquad 2w_1w_k - w_k$

For $i = 1$; $k = N$: $\qquad\qquad 2w_1w_N - w_1 - w_N$

For $1 < i < \; - 1$; $k = N$: $\qquad 2w_iw_N - w_i$

For $i = \; - 1$; $k = N$: $\qquad 2w_{N-1}w_N - w_{N-1} - 1$

— Factors for other covariances

For $1 < i$; $i + 1 < k < N$: $\qquad 2w_iw_k$

For $1 < i$; $i + 1 = k < N$: $\qquad 2w_iw_{i+1} - 1$

Note that covariances are symmetric, i.e. $u(w_i,w_k) = u(w_k,w_i)$, and so are the factors in Equation (D.4).

As an example, a natural gas simulate is used:

Component 1: carbon dioxide (CO_2)

Component 2: nitrogen (N_2)

Component 3: ethane (C_2H_6)

Component 4: methane (CH_4)

For an initial composition of $w_1 = w_2 = w_3 = 0,1$ and $w_4 = 0,7$, the variance/covariance matrix is obtained as follows.

$$U = \left(\frac{u}{m_{tot}}\right)^2 \begin{pmatrix} 1,82 & -1,08 & -0,08 & -0,66 \\ -1,08 & 2,02 & -0,98 & 0,04 \\ -0,08 & -0,98 & 2,02 & -0,96 \\ -0,66 & 0,04 & -0,96 & 1,58 \end{pmatrix} \qquad (D.5)$$

The variances for the component gases CO_2, N_2, C_2H_6, CH_4 and the covariances between any two of these depend on the filling sequence, i.e. they could be different with another filling sequence for the same composition.

As explained in D.2.1, instead of the variance/covariance matrix, the correlation matrix may be used together with the standard uncertainties of the mass fractions. For the data above, the correlation matrix is given by

$$R = \begin{pmatrix} 1,00 & -0,56 & -0,04 & -0,40 \\ -0,56 & 1,00 & -0,49 & 0,02 \\ -0,04 & -0,49 & 1,00 & -0,54 \\ -0,40 & 0,02 & -0,54 & 1,00 \end{pmatrix} \qquad (D.6)$$