
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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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.

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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 component 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, $1/V_{\text{mol}}$, as follows.

$$Z(V_{\text{mol}}, T) = 1 + \frac{B(T)}{V_{\text{mol}}} + \frac{C(T)}{V_{\text{mol}}^2} + \dots \quad (1)$$

$$Z(p, T) = 1 + B'(T)p + C'(T)p^2 + \dots \quad (2)$$

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	$1/\text{Pa}$
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	$1/\text{Pa}^2$
D	dilution factor	1
f	mixing factor	1
ϕ	volume fraction	1
i	gas mixture components ($i = 1, 2, \dots, N$)	—
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
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
U	variance/covariance matrix
$v(P)$	relative standard uncertainty of quantity P

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4 Basic principles

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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 $x(\text{H}_2) = 0,1$.

EXAMPLE 2 The sulfur dioxide content in air at 101,325 kPa and 25 °C, expressed by mass concentration, is $\beta(\text{SO}_2) = 1 \text{ mg/m}^3$.

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, $n_1, n_2, \dots, n_N$, the mole fraction x_i of any component i is given by

$$x_i = \frac{n_i}{\sum_k n_k} \quad (3)$$

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

$$w_i = \frac{m_i}{\sum_k m_k} \quad (4)$$

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

$$\phi_i = \frac{V_i}{\sum_k V_k} \quad (5)$$

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

$$c_i = \frac{n_i}{V_S} \quad (6)$$

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

$$\beta_i = \frac{m_i}{V_S} \quad (7)$$

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

$$\sigma_i = \frac{V_i}{V_S} \quad (8)$$

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)

$$n = \frac{m}{M} \quad (9)$$

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).

$$n = \frac{pV}{ZRT} \quad (10)$$

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):

$$m = \rho V \quad (11)$$

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

$$\rho Z = \frac{Mp}{RT} \quad (12)$$

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.

$$n_S = \sum_k n_k \quad (13)$$

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

$$m_S = \sum_k m_k \quad (14)$$

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:

$$V_S = f_S \sum_k V_k \quad (15)$$

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