Raad voor Accreditatie (Dutch Accreditation Council RvA)

Conversion between mole fractions and volume fractions in gas analysis

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Contents

1   Introduction

This document is a total revision of the previous version (July 1999), due to publication of the draft of the ISO standard 14912.

Like in many national regulations or legislations, it is stipulated in the Dutch vehicle-legislation (APK - in force since 1 January 1998) that in the testing and inspection of exhaust gas analysers, traceable gas mixtures are to be used. In addition, the composition of the required gas mixtures should be expressed in terms of **volume fractions**.

Traceable, is referring to established links between the required gas mixtures and accepted (inter) national measurement standards for gas mixture composition. The traceability of gas composition measurements is generally obtained by calibrating a comparison method with reference gas mixtures for which traceability to these (inter) national gas composition standards has been established. Due to the preparation method, the composition of these gas composition standards is expressed in terms of mole fractions. The mole fractions are calculated from the mass fractions using the molar mass of each analyse in the mixture. Consequently, the certified fractions in all related gas mixtures that are used in the testing and inspection of the analysers are originally stated in terms of **mole fractions**.

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 content of every analyte in the mixture and the composition of the complementary gas.

This guidance document is focussed on conversions between mole fractions and volume fractions for those gas mixtures for which underlined complete composition data is available.
Expressions in terms of volume fractions depend on the state conditions, i. e. pressure and temperature. This requires specification of the state conditions and mathematical tools to perform conversions between different state conditions.

As a crude approximation, mole <> volume conversions 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 either the compression factor or the density of the gas mixture. This guidance document will focus on the use of compression factors.

Conversion of quantities of composition is currently part of the work programme of Technical Committee ISO TC-158 -Gas Analysis. A working draft for ISO Standard 14912: Gas analysis - Quantities of Composition [1] has been prepared. It is assumed that is it not likely that equations used in the current draft will change much. This means that these equations can be applied for the purpose of this document.

2 Terms and definitions

The mole fraction or amount-of-substance fraction $x(X)$, is the quotient of the amount of substance of component X and the sum of the amounts of substance of all components of the gas mixture.
NOTE- the mole fraction is independent of pressure and temperature of the gas mixture.

The volume fraction $\phi(X)$, is the quotient of the volume of a component X and the sum of the volumes of all components of the 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 pressure and temperature have to be specified.

Compression factor Z, is the 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 - 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.

Virial coefficients, coefficients in the expansion of the compression factor in terms of powers of a quantity of state.

3 Conversions

Mole fraction $x_i \rightarrow$ **Volume fraction** ϕ_i using compression factors:

$$\phi_i = \frac{Z_i \cdot x_i}{\sum_{k=1}^{N} Z_k \cdot x_k} \quad (1)$$

Volume fraction $\phi_i \rightarrow$ **Mole fraction** x_i using compression factors:

$$x_i = \frac{\phi_i / Z_i}{\sum_{j=1}^{N} \phi_j / Z_j} \quad (2)$$

With:

$Z_{i, k}$ = compression factor of component $X_{i, k}$, at specified state conditions (temperature and pressure)

$\phi_{i, k}$ = volume fraction of component $X_{i, k}$

$x_{i, k}$ = mole fraction of component $X_{i, k}$

N = number of components in the mixture

It is important to incorporate all contributing components in the summation, including the balance gas!

Compression factor (*Z*)

Data on compression factors at various specified state conditions (p,T) is generally not available, but can be calculated from tabulated virial coefficients. For most pure gases the compression factor at room temperature and atmospheric pressure differs only moderately from unity.

In the following table, the difference, (1-*Z*), for a variety of gases at pressures below 2 bar and temperatures between 0 ºC and 30 ºC is given:

$-1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$3 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$1 \cdot 10^{-1}$
H_2	CO	Ar	CH_4	BF_3	C_2H_2	Cl_2	C_3H_8	C_4H_6
He	N_2	NO	Kr	CF_4	C_2H_4	C_3H_4	SO_2	C_4H_8
Ne	Air	O_2		CO_2	C_2H_6	C_3H_6		C_4H_{10}
				N_2O	HCl	NH_3		
				SiH_4	H_2S	SF_6		
				Xe				

In references [2], [3] and [4], compressions data can be found for pure gases occurring as natural gas components at two different state conditions.

When compression factors, if available at all in gas data compilations, are tabulated for selected reference conditions only, an important tools for estimating the compression factor of a pure gas at different state conditions, far away from the condensation region, are the following virial expansions:

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ... \qquad (3)$$

$$Z = 1 + B'p + C'p^2 + ... \qquad (4)$$

where the quantity of state is either the inverse molar volume, $1/V_m$, or the pressure p,

For a pure gas the compression factor can be calculated approximately from the second pressure virial coefficient, B', truncated after the linear term:

$$Z(p,T) = 1 + B'(T) \cdot p \qquad (5)$$

where   Z(p,T)   compression factor at pressure p and temperature T

       B´(T)   second pressure virial coefficient at temperature T

Equation (5) is applicable at state conditions where the density of the gas is less than 50 % of its critical density [5].

In the temperature range between 0 ^{0}C and 30 ^{0}C the virial coefficient B´(T) can be calculated approximately by linear interpolation as follows:

$$B'(T) = B'_0 + (B'_{30} - B'_0) \cdot \frac{(T-273,15)}{30} \qquad (6)$$

where: B´$_0$ second pressure virial coefficient at 0 ^{0}C

       B´$_{30}$ second pressure virial coefficient at 30 ^{0}C

An extensive compilation of second pressure virial coefficients at 0 ^{0}C and 30 ^{0}C is contained in ref. 4. In ref. 6, among others, a large amount of experimental gas data has been compiled in the format of parameters of empirical equations by which the second molar-volume virial coefficients B(T) can be calculated approximately over specified temperature ranges. Other sources of molar-volume virial coefficient data are refs.3 and 7.

For use in equation (5), molar-volume virial coefficients B(T) have to be converted to pressure virial coefficients B´(T) as follows:

$$B'(T) = \frac{B(T)}{R \cdot T}$$

4   Conversions and Uncertainties

Conversions of gas composition units involve complicated mathematics for the propagation of the uncertainties. Also the availability of data is limited. Uncertainties on compression factors are often based upon the reported number of digits. In ISO 14912 the general approach is described and the Standard comes with a software package. The input data for a number of uncertainty estimates can be taken from a wide range of ISO standards, which are generally accepted in the domain of gas analysis.
In this guidance document a number of conversion examples are given which reflect a number of gas compositions for which accreditation was granted.

Examples

Conversions according to equation 1, for two state conditions

	Mole fraction (mol/mol)	Z (15 ºC , 1 bar)	Z (0 ºC , 1,0135 bar)	Volume fraction (15 ºC , 1 bar) (vol/vol)	Volume fraction (0 ºC , 1,0135 bar) (vol/vol)
CO	0,034780	0,9996	0,999331	0,034804	0,034806
CO_2	0,140800	0,9943	0,993272	0,140152	0,140049
C_3H_8	0,002038	0,9823	0,978853	0,002004	0,001998
N_2	0,822382	0,9997	0,999524	0,823040	0,823147

Conversions according to equation 2, for two state conditions

	Volume fraction (15 ⁰C , 1 bar) (vol/vol)	Z (15 ⁰C , 1 bar)	Mole fraction (mol/mol)
CO	0,060000	0,9996	0,059955
CO_2	0,148000	0,9943	0,148677
C_3H_8	0,002400	0,9823	0,002440
N_2	0,789600	0,9997	0,788928

	Volume fraction (0 ⁰C , 1,0135 bar) (vol/vol)	Z (0 ⁰C , 1,0135 bar)	Mole fraction (mol/mol)
CO	0,060000	0,999331	0,059952
CO_2	0,148000	0,993272	0,148784
C_3H_8	0,002400	0,978853	0,002448
N_2	0,789600	0,999524	0,788816

Data for compression factor Z at 15 ⁰C , 1 bar, were taken from references [8,9]

The uncertainty in the compression factors of the pure gases mentioned above can be roughly estimated from the calculations according to ISO Standard 14912.

Applying the equations on the above mixtures, assuming a relative standard uncertainty of 0,5 % on each analyte in the mixture, yields to an increase of approximately 0,1 % relative when converting from mole fractions to volume fractions.

5   References:

1) ISO 14912 Gas Analysis – Quantities of Composition 6 [th] working draft (March 1999).

2) ISO 6976 Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition.

3) Humphreys, A. E., "Some Thermophysical Constants of Components of Natural Gas and   Cognate Fluids", GERG Technical Monograph No. TPC/1 (1986).

4)   DIN 1871 Gaseous fuels and other gases - Density and other volumetric quantities.

5)   Reid, R. C., Prausnitz, J. M., Poling, B. E., "The Properties of Gases and Liquids", 4th Edition, New York, McGraw Hill, 1987

6) Daubert, T. E., Danner, R. P., "Physical and Thermodynamic Properties of Pure Chemicals", New York, Hemisphere, 1989

7) Dymond, J. H., Smith, E. B., "The Virial Coefficients of Pure Gases and gas Mixtures", Oxford, Clarendon Press, 1980

8) Encyclopédie des Gaz; Air Liquide, Elsevier Scientific 1976; ISBN 0-444-41492-4

9) Messer Griesheim; Gase handbuch, 3. Auflage, 1989

Suggested reading:

Atomic weights of the elements 1993, IUPAC, Commission on Atomic Weights and Isotopic abundances, Pure & Appl. Chem. Vol.66, No12, pp 2423 - 2444, 1994

6 Modification compared to previous revision

Compared to the previous revision of this document the following modifications are included:
- New format;
- NKO replaced by RvA.