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Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition

Gaz naturel — Calcul du pouvoir calorifique, de la masse volumique, de la densité relative et de l'indice de Wobbe à partir de la composition

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Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 6976 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 01, *Analysis of natural gas*.

This third edition cancels and replaces the second edition (ISO 6976:1995), which has been technically revised.

Introduction

Both international and intra-national custody transfer of natural gas usually require precise determination of both the quantity and the quality of the gas to be traded. This International Standard specifies methods for the calculation of key properties that describe gas quality, namely gross and net calorific value, density, relative density, and gross and net Wobbe index. The methods provide the means of calculating these properties and their uncertainties, for any natural gas, natural gas substitute, or similar combustible gaseous fuel of known composition at commonly used reference conditions.

Values of the various properties calculated in accordance with this third edition of ISO 6976 will, in general, differ only by very small amounts from those calculated using the second (1995) edition of this standard. In this context it is recognised that:

- (a) Adoption of the revisions detailed in this edition will not be without cost, since instrumental software will need updating;
- (b) Recorded energy content and hence billed energy will, in consequence of these revisions, change by small amounts;
- (c) Unintended impacts could occur if the revisions are implemented uncritically - for instance, if the revisions are implemented at input points to a pipeline system but not at exit points, then a costly accountancy imbalance may result; and
- (d) Commercial, contractual, regulatory and legislative obligations will need to be taken into account.

For these reasons, and depending upon the user's application, it may be appropriate to undertake an impact assessment in order to determine an agreed timing and procedure for implementation of the provisions of this edition of ISO 6976.

Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition

1 Scope

This International Standard specifies methods for the calculation of gross calorific value, net calorific value, density, relative density, gross Wobbe index and net Wobbe index of natural gases, natural gas substitutes and other combustible gaseous fuels, when the composition of the gas by mole fraction is known. The methods specified provide the means of calculating the properties of the gas mixture at commonly used reference conditions.

For the purpose of this International Standard the input mole fractions shall sum to unity exactly. Guidance on the achievement of this requirement is available in ISO 6974-1 and ISO 6974-2. All components with mole fractions greater than 0,000 05 shall be accounted for.

If the composition of the gas is known by volume fractions, these shall first be converted to mole fractions in accordance with ISO 14912 (subclause 5.1.2). Note, however, that these derived mole fractions will have uncertainties greater than those of the original volume fractions.

The methods of calculation require values for various physical properties of the pure components; these values, together with associated uncertainties, are provided in tables and their sources are identified.

Methods are given for estimating the uncertainties of calculated properties.

The methods of calculation of the values of properties on either a molar, mass or volumetric basis are applicable to any natural gas, natural gas substitute or other combustible fuel that is normally gaseous, except that for properties on the volumetric basis the method is restricted to mixtures for which the compression factor at reference conditions is greater than 0,9.

Example calculations are given in annex D for the recommended methods of calculation.

NOTE 1 The qualifiers "superior", "higher", "upper" and "total" are, for the purposes of this International Standard, synonymous with "gross"; likewise, "inferior" and "lower" are synonymous with "net". The term "heating value" is synonymous with "calorific value"; "mass density" and "specific density" are synonymous with "density"; "specific gravity" is synonymous with "relative density"; "Wobbe number" is synonymous with "Wobbe index"; "compressibility factor" is synonymous with "compression factor". The dimensionless quantity molecular weight is numerically equal to the molar mass in $\text{kg}\cdot\text{kmol}^{-1}$.

NOTE 2 For aliphatic hydrocarbons of carbon number 7 or above, any isomer present at a mole fraction greater than 0,000 05 should be included with the normal isomer of the same carbon number.

NOTE 3 If the user's requirement includes the replacement of, for example, a C6+ or C7+ grouping of analytically unresolved components by a single pseudo-component, then it shall be the user's own task to set the mole fraction composition, and hence properties, of this pseudo-component so as to be fit for purpose in the particular application. So-called 'spectator water' and 'non-combustible hydrogen sulfide' may also be treated as pseudo-components by setting the appropriate enthalpy of combustion values to zero.

NOTE 4 There are no explicit limits of composition to which the methods described in this International Standard are applicable. However, the restriction of volumetric basis calculations to mixtures with compression factor greater than 0,9 at reference conditions sets implicit limits on composition.

NOTE 5 Because the mole fraction of any water present is not normally available from chromatographic analysis, it is common practice to calculate the physical properties on a dry gas basis and to allow for the effects of water vapour in a separate procedure. However, if the mole fraction of water vapour is known then the property calculations can be carried out completely in accordance with the procedures described herein. The effects of water vapour on calorific value, whether the latter is directly measured or calculated, are discussed in ISO Technical Report TR 29922 [1].

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6974-1:2013, *Natural gas – Determination of composition and associated uncertainty by gas chromatography – Part 1: General guidelines and calculation of composition*

ISO 6974-2:2013, *Natural gas – Determination of composition and associated uncertainty by gas chromatography – Part 2: Uncertainty calculations*

ISO 14912:2003, *Gas analysis – Conversion of gas mixture composition data*

ISO/IEC Guide 99-12:2007, *International vocabulary of metrology - Basic and general concepts and associated terms (VIM)*, Joint Committee for Guides in Metrology, JCGM 200:2008 (BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML), 90+xii p.

3 Terms and definitions

For the purposes of this International Standard, definitions of terms relating to metrology (uncertainty, accuracy, precision, trueness, bias, repeatability and reproducibility) shall be taken from VIM.

In addition, the following definitions apply.

3.1
gross calorific value
amount of heat that would be released by the complete combustion with oxygen of a specified quantity of gas, in such a way that the pressure p_1 at which the reaction takes place remains constant, and all the products of combustion are returned to the same specified temperature t_1 as that of the reactants, all of these products being in the gaseous state except for water, which is condensed to the liquid state at t_1

NOTE Where the quantity of gas is specified on a molar basis, the gross calorific value is designated as $(Hc)_G(t_1, p_1)$; on a mass basis the gross calorific value is designated as $(Hm)_G(t_1, p_1)$. Where the quantity of gas is specified on a volumetric basis, the gross calorific value is designated as $(Hv)_G(t_1, p_1; t_2, p_2)$, where t_2 and p_2 are the gas volume (metering) reference conditions (see Figure 1).

3.2
net calorific value
amount of heat that would be released by the complete combustion with oxygen of a specified quantity of gas, in such a way that the pressure p_1 at which the reaction takes place remains constant, and all the products of combustion are returned to the same specified temperature t_1 as that of the reactants, all of these products being in the gaseous state

NOTE On molar, mass and volumetric bases, the net calorific value is designated respectively as $(Hc)_M(t_1, p_1)$, $(Hm)_N(t_1, p_1)$ and $(Hv)_N(t_1, p_1; t_2, p_2)$.

3.3
density
mass of a gas sample divided by its volume at specified conditions of pressure and temperature

3.4
relative density
density of a gas divided by the density of dry air of reference composition at the same specified conditions of pressure and temperature

NOTE The term ideal relative density applies when both gas and air are considered as gases that obey the ideal gas law (see 3.8); the term real relative density applies when both gas and air are considered as real fluids (see 3.9). For the fixed reference composition of dry air, see ISO Technical Report TR 29922 [1].

3.5**gross Wobbe index**

volumetric-basis gross calorific value, at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions

NOTE In common usage, and in the absence of any other qualifier, the term Wobbe index is taken to mean the quantity that is here identified as gross Wobbe index.

3.6**net Wobbe index**

volumetric-basis net calorific value, at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions

3.7**enthalpy of transformation**

amount of heat release that accompanies the change in condition (transformation) of a substance or system from one (initial) condition to another (final) condition

NOTE 1 A *positive* heat release is represented by thermodynamic convention as a numerically equal *negative* increment of enthalpy.

NOTE 2 In the context of this International Standard the following may be identified :

enthalpy of combustion – in this case the initial condition is that of an unburned stoichiometric mixture of reactants and the final condition is that of the products of combustion at the same temperature and pressure,

standard enthalpy of vaporization – here the initial condition is that of a substance in the liquid state at saturation and the final condition is that of the same substance in the hypothetical state of the ideal gas at the same temperature,

enthalpy (or enthalpic) difference – here the initial condition is that of a gas or gas mixture at temperature T_1 and the final condition is that of the same gas or gas mixture at the same pressure but at a different temperature T_2 , and

enthalpy (or enthalpic) correction (residual enthalpy) – here the initial condition is that of a gas or gas mixture in the hypothetical state of an ideal gas and the final condition is that of the same gas or gas mixture at the same temperature and pressure in the state of the real gas.

3.8**ideal gas**

gas which obeys the ideal gas law

NOTE The ideal gas law may be expressed as

$$p \cdot V^o = R \cdot T \quad (1)$$

where

p is the absolute pressure;

T is the thermodynamic temperature;

V^o is the volume occupied by one mole of ideal gas (ideal molar volume), and

R is the gas constant in coherent units

3.9**real gas**

gas which deviates from volumetric ideality

NOTE No real gas obeys the ideal gas law. Deviations from volumetric ideality may be written in terms of the equation of state

$$p \cdot V = Z(p, T) \cdot R \cdot T \quad (2)$$

where

V is the volume occupied by one mole of the real gas (real molar volume), and

$Z(T,p)$ is a variable, often close to unity, and is known as the compression factor (see 3.10).

3.10 compression factor

actual (real) volume of a given amount of gas at a specified pressure and temperature divided by its volume under the same conditions as calculated from the ideal gas law

3.11 combustion reference conditions

specified temperature t_1 and pressure p_1 at which the fuel is notionally burned

3.12 metering reference conditions

specified temperature t_2 and pressure p_2 at which the volume of fuel to be burned is notionally determined

NOTE 1 There is no *a priori* reason for the metering reference conditions to be the same as the combustion reference conditions (see Figure 1).

NOTE 2 A range of reference conditions is in use throughout the world.

NOTE 3 Throughout this standard the use of 15,55 °C is intended as shorthand for the exact Celsius equivalent of 60 °F i.e. $15\frac{5}{9}$ or 15,55 (recurring) °C.

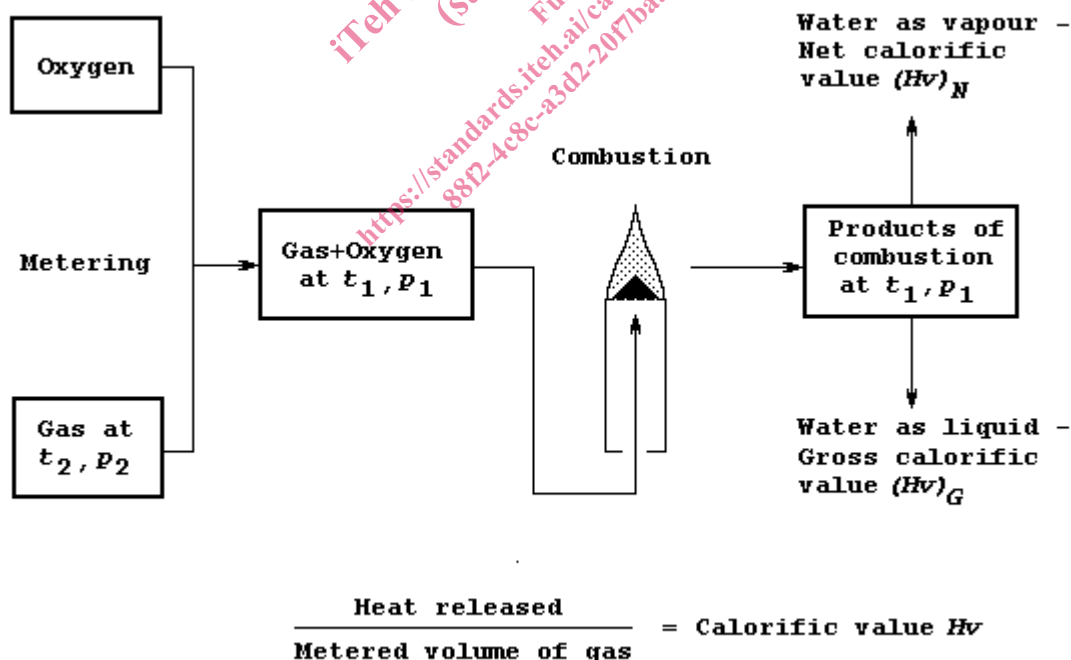


Figure 1 —Calorific value on a volumetric basis - metering and combustion reference conditions

4 Symbols and units

4.1 Quantities

Symbol	Meaning	Unit
<i>A</i>	atomic mass	kg·kmol ⁻¹
<i>a</i>	atomic index for carbon in the generalised molecular species C _a H _b N _c O _d S _e	-
<i>b</i>	atomic index for hydrogen in the generalised molecular species C _a H _b N _c O _d S _e	-
<i>c</i>	atomic index for nitrogen in the generalised molecular species C _a H _b N _c O _d S _e	-
<i>D</i>	density	kg·m ⁻³
<i>d</i>	atomic index for oxygen in the generalised molecular species C _a H _b N _c O _d S _e	-
<i>e</i>	atomic index for sulfur in the generalised molecular species C _a H _b N _c O _d S _e	-
<i>F</i>	function that generates property <i>Y</i>	-
<i>G</i>	relative density	-
<i>Hc</i>	molar-basis calorific value	kJ·mol ⁻¹
<i>Hm</i>	mass-basis calorific value	MJ·kg ⁻¹
<i>Hv</i>	volumetric-basis calorific value	MJ·m ⁻³
<i>k</i>	coverage factor	-
<i>L</i>	molar enthalpy of vaporization of water	kJ·mol ⁻¹
<i>M</i>	molar mass	kg·kmol ⁻¹
<i>N</i>	number of components in a mixture	-
<i>n</i>	number of determinations in a set of values	-
<i>p</i>	pressure (absolute)	kPa
<i>q</i>	exact input quantity for calculation of <i>Y</i>	(varies)
<i>R</i>	molar gas constant	J·mol ⁻¹ ·K ⁻¹
<i>r</i>	correlation coefficient	-
<i>s</i>	summation factor	-
<i>T</i>	thermodynamic (absolute) temperature	K
<i>t</i>	Celsius temperature	°C
<i>U(Y)</i>	expanded uncertainty of <i>Y</i>	(varies)
<i>u(Y)</i>	standard uncertainty of <i>Y</i>	(varies)
<i>V</i>	molar volume	m ³ ·mol ⁻¹
<i>W</i>	Wobbe index	MJ·m ⁻³
<i>x</i>	mole fraction	-
<i>Y</i>	general (unspecified) physical property	(varies)
<i>y</i>	inexact input quantity for calculation of <i>Y</i>	(varies)
<i>Z</i>	compression factor	-

4.2 Subscripts

Symbol	Meaning
<i>G</i>	gross (calorific value or Wobbe index)
<i>i</i>	serial counter component identifier
<i>j</i>	serial counter component identifier
<i>k</i>	serial counter
<i>m</i>	serial counter
<i>N</i>	net (calorific value or Wobbe index)
<i>n</i>	serial counter
<i>air</i>	for air
1	combustion reference state
2	metering reference state

4.3 Superscript

Symbol	Meaning
o	for the ideal gas state

5 Principle

Methods are provided for the calculation of the calorific values (gross and net), density, relative density and Wobbe indices (gross and net) of any natural gas, natural gas substitute or other combustible gaseous fuel from a known molar composition.

For calorific values, these methods use equations in which, for all individual molecular species of the gas mixture, the tabulated ideal-gas molar-basis gross calorific value is weighted in accordance with its mole fraction, all terms then being added together to obtain the "mole fraction average" of this quantity for the ideal gas mixture on a molar basis. Further equations are given that convert this quantity into the ideal-gas net calorific value, and then into the ideal-gas gross and net calorific values on either a mass basis or a volumetric basis.

Likewise, for density and relative density, the methods use equations in which, for all individual molecular species of the gas mixture, the tabulated value of molar mass is weighted in accordance with its mole fraction, all terms then being added together to obtain the mole fraction average of this quantity. Equations are given that convert this mole fraction average molar mass into the ideal-gas density or relative density.

Values of the density and relative density for the real gas are then obtained by the application of a volumetric correction factor (compression factor), a prescription for the calculation of which is given.

For calorific values, conversion from the ideal-gas state to the real-gas state is in principle slightly less simple. The application should first be made of a small enthalpic correction (residual enthalpy) to the calorific value (gross or net) of the ideal gas on the molar basis, so as to obtain the calorific value of the real gas on the molar basis. For the purposes of this standard, however, this enthalpic correction has been estimated as so small as to be justifiably negligible (see ISO TR 29922 [1]).

In consequence of neglecting the enthalpic correction, the real-gas calorific values on the molar and mass bases are in effect set as equal to the corresponding ideal-gas values. To obtain the values of the real-gas

calorific values (gross or net) on the volumetric basis from the corresponding ideal-gas values, however, the volumetric correction factor (compression factor) mentioned above has to be applied.

Finally, equations are given for the calculation of Wobbe indices, for either the ideal gas or real gas, from the other properties considered herein.

In clause 12 tabulated values are given for the relevant physical properties of the pure components of natural gas for each of the commonly used reference conditions. Example calculations are given in annex D.

6 Behaviour of ideal and real gases

6.1 Enthalpy of combustion

The most fundamental physical quantities required in the calculation of calorific values from first principles are the ideal-gas (standard) molar enthalpies of combustion (ideal molar calorific values) for the pure component gases. These quantities are complex functions of temperature; thus, the values required depend upon the combustion reference temperature t_1 . For practical reasons, it is not intended that the user should carry out calculations that give the appropriate values at any arbitrary combustion reference temperature. Instead, tabulations are given for the temperatures $t_1 = 25\text{ °C}$, 20 °C , $15,55\text{ °C}$ (60 °F , see Note 3 to definition 3.12), 15 °C (59 °F) and 0 °C . The derivations of the values listed in clause 12 table 3 are discussed in ISO TR 29922 [1]; the important point is that all five values for any substance are mutually consistent from a thermodynamic perspective.

6.2 Calculation of compression factor

For any volumetric-basis calorific value, a real-gas correction is required to account for the deviation of the real gas from volumetric ideality. This correction is not negligible, and is also required in the calculation of density, relative density and Wobbe index. ISO TR 29922 [1] discusses the background to the way in which corrections for volumetric non-ideality shall be applied, discusses the principles involved, and justifies the simplifications employed which enable tractable calculations, as detailed below (equation (3)), to be made.

This correction for volumetric non-ideality is made through use of the compression factor Z of the mixture. The formulation to be used for Z at the metering reference conditions, as required for the calculations described in clauses 7 to 10 of this International Standard, is (see [1])

$$Z(t_2, p_2) = 1 - \left(\frac{p_2}{p_o} \right) \times \left[\sum_{j=1}^N x_j \cdot s_j(t_2, p_o) \right]^2 \quad (3)$$

where $p_o = 101,325\text{ kPa}$ ($14,695\text{ 95 psi}$), and the metering reference pressure p_2 is expressed in the same units. The summation is taken over all N components of the mixture and the equation is valid for the range $90 < p_2/\text{kPa} < 110$ ($13,05 < p_2/\text{psi} < 15,95$). Values of the so-called summation factor $s_j(t_2, p_o)$ are given in clause 12 table 2 at the four metering reference temperatures of common interest, for all of the components of natural gas and substitute natural gas considered in this International Standard. The derivations of these values are detailed in ISO TR 29922 [1].

NOTE Equation (3) may also be used to calculate values of compression factor of pure components, but this will not necessarily give the most accurate result possible. In particular, the equation will not provide acceptable values for the compression factors of hydrogen, helium or neon, for which $Z > 1$, nor for any components, such as the higher hydrocarbons, that are not gaseous at the metering reference conditions. The user should consider the fitness-for-purpose of any such calculation before its use outside of the context of this International Standard. Definitive values of compression factor for several pure components, namely the so-called permanent gases, are given in ISO TR 29922 [1].