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Natural gas — Calculation of calorific values, density, relative density and Wobbe index 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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Annexes

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.

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.

International Standard ISO 6976 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition cancels and replaces the first edition (ISO 6976:1983), of which it constitutes a technical revision.

Annexes A and B form an integral part of this International Standard. Annexes C, D, E, F, G, H, J, K, L and M are for information only.

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

1 Scope

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

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

Methods are given for estimating the precision of calculated properties.

The methods of calculation of the values of properties on either a molar or mass basis are applicable to any dry natural gas, natural gas substitute or other combustible fuel which is normally gaseous. For the calculation of the values of properties on a volumetric basis, the methods are restricted to gases consisting preponderantly of methane (not less than 0,5 mole fraction).

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

NOTES

1 The symbols used in this International Standard, together with their meanings, are given in annex A.

2 The qualifiers "higher", "upper", "total" and "gross" are, for the purposes of this International Standard, synonymous with "superior"; likewise, "lower" and "net" are synonymous with "inferior". The term "heating value" is synonymous with "calorific value"; "specific gravity" is synonymous with "relative density"; "Wobbe number" is synonymous with "Wobbe index"; "compressibility factor" is synonymous with "compression factor".

3 If the composition of the gas is known by volume fractions these must be converted to mole fractions (see annex C). Note, however, that the derived mole fractions will have uncertainties greater than those of the original volume fractions.

4 For the purposes of this International Standard, the sum of the mole fractions used must be unity to the nearest 0,000 1, and all components with mole fractions greater than 0,000 05 must be accounted for.

5 For the calorific value calculated on a volumetric basis, there are limitations on the amounts of components other than methane which may be present. It is impossible to be definitive on this matter, but the following guidelines may be useful:

N_2 should not be present in amounts exceeding 0,3 mole fraction;

CO_2 and C_2H_6 should each not exceed 0,15 mole fraction;

no other component should exceed 0,05 mole fraction.

Given these limits, the expected trueness of the calculation is within 0,1 %.

6 The effects of water vapour on the calorific value, either directly measured or calculated, are discussed in annex F.

7 For the methods of calculation described to be valid, the gas must be above its hydrocarbon dew-point at the prescribed reference conditions.

8 The values of basic physical property data are subject to revision as more accurate values become available from authoritative sources.

2 Definitions

For the purposes of this International Standard, the following definitions apply.

2.1 superior calorific value: The amount of heat which would be released by the complete combustion in air 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 formed by combustion, which is condensed to the liquid state at t_1.

Where the quantity of gas is specified on a molar basis, the calorific value is designated as $\overline{H}_S(t_1,p_1)$; on a mass basis the calorific value is designated as $\hat{H}_S(t_1,p_1)$.

Where the quantity of gas is specified on a volumetric basis, the calorific value is designated as $\tilde{H}_S[t_1,p_1, V(t_2,p_2)]$, where t_2 and p_2 are the gas volume (metering) reference conditions (see figure 1).

2.2 inferior calorific value: The amount of heat which would be released by the complete combustion in air 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.

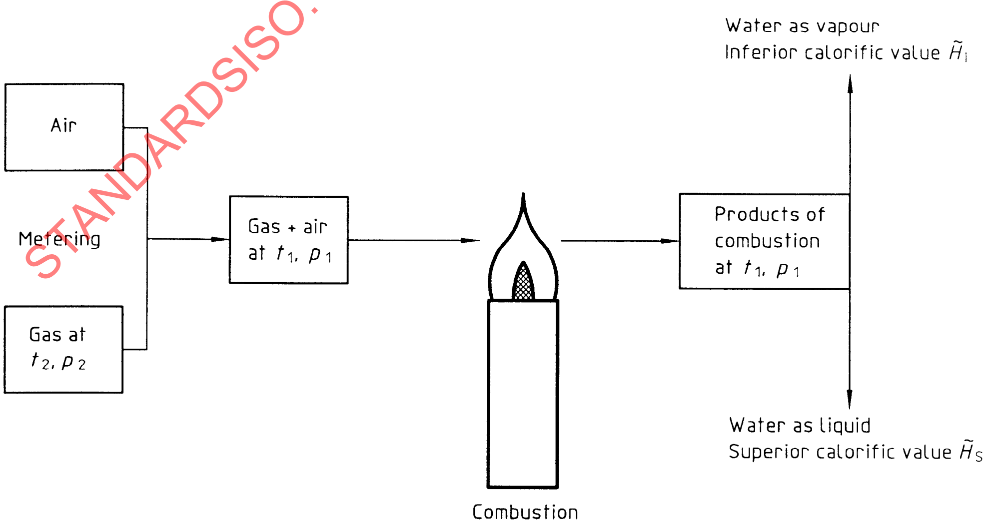
On molar, mass and volumetric bases, the inferior calorific value is designated respectively as $\overline{H}_I(t_1,p_1)$, $\hat{H}_I(t_1,p_1)$ and $\tilde{H}_I[(t_1, p_1),V(t_2,p_2)]$.

2.3 density: The mass of a gas sample divided by its volume at specified conditions of pressure and temperature.

2.4 relative density: The density of a gas divided by the density of dry air of standard composition (see annex B) at the same specified conditions of pressure and temperature. The term ideal relative density applies when both gas and air are considered as fluids which obey the ideal gas law (see 2.7); the term real relative density applies when both gas and air are considered as real fluids.

2.5 Wobbe index: The superior calorific value on a volumetric basis at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions.

2.6 enthalpy of transformation: The enthalpy of transformation of a substance from state A to state B is thermodynamic terminology for the amount of heat release which accompanies the transformation between states. A **positive** heat release is taken by convention to be a numerically identical **negative** enthalpy increment. The quantities enthalpy of combustion and enthalpy of vaporization therefore have meanings which should be contextually self-evident; the term enthalpic correction refers to the (molar) enthalpy of transformation between the ideal and real states of a gas.



$$\frac{\text{Heat release}}{\text{Metered volume of gas}} = \text{Calorific value } \tilde{H}$$

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

2.7 ideal gas and real gas: An ideal gas is one which obeys the ideal gas law:

$$p \cdot V_{\mathrm{m}} = R \cdot T \qquad \ldots (1)$$

where

p is the absolute pressure;

T is the thermodynamic temperature;

V_{m} is the volume per mole of gas;

R is the molar gas constant, in coherent units.

No real gas obeys this law. For real gases, equation (1) must be rewritten as

$$p \cdot V_{\mathrm{m}} = Z(T,p) \cdot R \cdot T \qquad \ldots (2)$$

where $Z(T,p)$ is a variable, often close to unity, and is known as the compression factor (see 2.8 and E.2).

2.8 compression factor: The actual (real) volume of a given mass of gas at a specified pressure and temperature divided by its volume, under the same conditions, as calculated from the ideal gas law.

2.9 combustion reference conditions: The specified temperature t_1 and pressure p_1. These are the conditions at which the fuel is notionally burned (see figure 1).

2.10 metering reference conditions: The specified temperature t_2 and pressure p_2. These are the conditions at which the amount of fuel to be burned is notionally determined; there is no *a priori* reason for these to be the same as the combustion reference conditions (see figure 1).

NOTE 9 A range of reference conditions is in use throughout the world; appropriate data for the principal sets of metric reference conditions are given in tables in this International Standard.

2.11 dry natural gas: Gas which does not contain water vapour at a mole fraction greater than 0,000 05.

3 Principle

Methods are provided for the calculation of the calorific values, density, relative density and Wobbe index of any dry natural gas, natural gas substitute or other combustible gaseous fuel from a known composition. These methods use equations in which, for all individual molecular species of the gas mixture, the values of ideal-gas thermophysical properties (which are given) are weighted in accordance with the corresponding mole fraction, all the terms then being added together to obtain the "mole fraction average" of the property for the ideal-gas mixture. Values on a volumetric basis are then converted to values for the real-gas state by applying a volumetric correction factor.

NOTE 10 An enthalpic correction factor which is also, in principle, required in calorific value calculations is deemed to be negligible in all relevant cases.

In clause 10, values are given for the physical properties of the pure components of natural gas on molar, mass and volumetric bases for the commonly used reference conditions. Examples of calculations are given in annex D.

4 Behaviour of ideal and real gases

4.1 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 for the component gases of the mixture. 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 himself carries out calculations which give the appropriate values at any arbitrary combustion reference temperature. Instead, tabulations are given for the temperatures $t_1 = 25$ °C, 20 °C, 15 °C and 0 °C. In clause E.1 the derivations of the values tabulated are discussed; the important point is that all four values for any substance are mutually consistent in a thermodynamic sense.

For the calorific value (on any of the three possible bases), a so-called enthalpic correction is, in principle, required in order to convert the ideal-gas enthalpy of combustion for the gas mixture to a value appropriate to the real gas. This, however, is generally small enough to be negligible. A discussion justifying such neglect is given in clause E.3.

4.2 Calculation of compression factor

For the volumetric-basis calorific value, a second real-gas correction is required to account for the deviation of the gas from volumetric ideality, and this is generally not negligible. This correction is also required in the calculation of density, relative density and, by implication, Wobbe index. Clause E.2 gives the background to the way in which corrections for volumetric non-ideality should be applied, discusses the principles involved, and justifies the simplifications employed which enable tractable calculations to be made without necessitating machine computation.

Such corrections for volumetric non-ideality are made using the compression factor Z_{mix}. The formulation to be used for Z_{mix} at the metering reference conditions, as required for the calculations described in clauses 5 to 9, is (equation E.17):

$$Z_{\text{mix}}(t_2,p_2) = 1 - \left[\sum_{j=1}^{N} x_j \cdot \sqrt{b_j} \right]^2 \qquad \ldots (3)$$

where the summation is taken over all N components of the mixture. Values of the so-called summation factor $\sqrt{b_j}$ are given in table 2 (clause 10) at the three metering reference conditions of common interest, for all of the components of natural gas and substitute natural gas considered in this International Standard. Values are also given for all pure component compression factors (or hypothetical compression factors) Z_j, from which the b_j's have generally been derived using the relationship $b_j = 1 - Z_j$. Any user requiring greater detail should consult clause E.2.

5 Calculation of calorific value on a molar basis

5.1 Ideal gas

The ideal-gas calorific value on a molar basis, at a temperature t_1, of a mixture of known composition is calculated from the equation

$$\overline{H}^{\mathrm{o}}(t_1) = \sum_{j=1}^{N} x_j \cdot \overline{H}_j^{\mathrm{o}}(t_1) \qquad \ldots (4)$$

where

$\overline{H}^{\mathrm{o}}(t_1)$ is the ideal molar calorific value of the mixture (either superior or inferior);

$\overline{H}_j^{\mathrm{o}}(t_1)$ is the ideal molar calorific value of component j (either superior or inferior);

x_j is the mole fraction of component j.

Numerical values of $\overline{H}_j^{\mathrm{o}}$ for $t_1 = 25$ °C are given in table 3 (clause 10); the values for $(\overline{H}_j^{\mathrm{o}})_{\mathrm{S}}$ are taken from the original literature sources cited in annex M, and the values for $(\overline{H}_j^{\mathrm{o}})_{\mathrm{I}}$ derived using the accepted value of the standard enthalpy of vaporization of water at 25 °C (see annex B).

Values for $\overline{H}_j^{\mathrm{o}}$ for other temperatures ($t_1 = 20$ °C, 15 °C and 0 °C) are also given in table 3; these values have been derived from the 25 °C values in accordance with the methods described in clause E.1.

NOTES

11 Values of $\overline{H}_j^{\mathrm{o}}$ are independent of pressure; consequently the combustion reference pressure p_1 is irrelevant for the ideal-gas case and is omitted from the nomenclature adopted.

12 The ideal-gas calorific value on a molar basis of a gas or gas mixture is defined in this International Standard as a positive number. The values given in table 3 are numerically equal to the standard molar enthalpies of combustion, which are, however, conventionally expressed as negative quantities (see 2.6).

5.2 Real gas

For the purposes of this International Standard the real-gas calorific value on a molar basis is taken as numerically equal to the corresponding ideal-gas value.

NOTE 13 A rigorous approach to the calculation of the real-gas calorific value on a molar basis from the ideal-gas value would require the calculation of an enthalpic correction (see 4.1) for the mixture. In practice, this correction is very small for typical natural gases, and can usually be neglected with resultant errors not exceeding 50 J·mol^{-1} (approximately 0,005 %) (see clause E.3).

6 Calculation of calorific value on a mass basis

6.1 Ideal gas

The ideal-gas calorific value on a mass basis, at a temperature t_1, of a mixture of known composition is calculated from the equation

$$\hat{H}^{\mathrm{o}}(t_1) = \frac{\overline{H}^{\mathrm{o}}(t_1)}{M} \qquad \ldots (5)$$

where

M is the molar mass of the mixture, and is calculated from the equation

$$M = \sum_{j=1}^{N} x_j \cdot M_j \qquad \ldots (6)$$

x_j being the mole fraction of component j;

M_j being the molar mass of component j;

$\hat{H}^\circ(t_1)$ is the ideal calorific value on a mass basis of the mixture (either superior or inferior).

Table 1 (clause 10) lists values of the molar mass for all components considered in this International Standard.

Use of equations (5) and (6) represents the definitive method for calculating $\hat{H}^\circ$. An alternative method uses the equation

$$\hat{H}^\circ(t_1) = \sum_{j=1}^{N}\left(x_j \times \frac{M_j}{M}\right)\hat{H}_j^\circ(t_1) \qquad \ldots (7)$$

where $\hat{H}_j^\circ(t_1)$ is the ideal calorific value on a mass basis of component j (either superior or inferior).

For convenience, values of $\hat{H}_j^\circ$ for four values of t_1 (25 °C, 20 °C, 15 °C and 0 °C) are given in table 4 (clause 10), in order that the user may avoid the necessity of using values of $\overline{H}_j^\circ$ as the starting point of a calculation.

Numerical values obtained from either method will be concordant to within 0,01 MJ·kg^{-1}, which is within the limits of significance for the current state-of-the-art.

6.2 Real gas

For the purposes of this International Standard, the real-gas calorific value on a mass basis is taken as numerically equal to the corresponding ideal-gas value.

NOTE 14 See 5.2 for clarification and justification.

7 Calculation of calorific value on a volumetric basis

7.1 Ideal gas

The ideal-gas calorific value on a volumetric basis, for a combustion temperature t_1, of a mixture of known composition, metered at a temperature t_2 and pressure p_2, is calculated from the equation

$$\tilde{H}^\circ[t_1,V(t_2,p_2)] = \overline{H}^\circ(t_1) \times \frac{p_2}{R \cdot T_2} \qquad \ldots (8)$$

where

$\tilde{H}^\circ[t_1,V(t_2,p_2)]$ is the ideal calorific value on a volumetric basis of the mixture (either superior or inferior);

R is the molar gas constant (= 8,314 510 J·mol^{-1}·K^{-1}, see clause B.1);

$T_2 (= t_2 + 273{,}15)$ is the absolute temperature, in kelvins.

The use of equation (8) represents the definitive method for calculating $\tilde{H}^\circ$. An alternative method uses the equation

$$\tilde{H}^\circ[t_1, V(t_2,p_2)] = \sum_{j=1}^{N} x_j \cdot \tilde{H}_j^\circ[t_1,V(t_2,p_2)] \qquad \ldots (9)$$

where $\tilde{H}_j^\circ[t_1,V(t_2,p_2)]$ is the ideal calorific value on a volumetric basis of component j (either superior or inferior).

For convenience, values of $\tilde{H}_j^\circ$ for a variety of combustion and metering reference conditions are given in table 5 (clause 10), in order that the user may avoid the necessity of using values of $\overline{H}_j^\circ$ as the starting point of a calculation.

Numerical values obtained from either method will be concordant to within 0,01 MJ·m^{-3}, which is within the limits of significance for the current state-of-the-art.

7.2 Real gas

The real-gas calorific value on a volumetric basis, for combustion at temperature t_1 and pressure p_1 of a gas mixture metered at a temperature t_2 and pressure p_2 is calculated from the equation

$$\tilde{H}[t_1,V(t_2,p_2)] = \frac{\tilde{H}^\circ[t_1,V(t_2,p_2)]}{Z_{\text{mix}}(t_2,p_2)} \qquad \ldots (10)$$

where

$\tilde{H}[t_1,V(t_2,p_2)]$ is the real-gas calorific value on a volumetric basis (either superior or inferior);

$Z_{\text{mix}}(t_2,p_2)$ is the compression factor at the metering reference conditions.

The compression factor $Z_{\text{mix}}(t_2,p_2)$ is calculated from equation (3), using values of the summation factor $\sqrt{b_j}$ given for individual pure substances in table 2 (clause 10).

NOTE 15 See 5.2 for clarification and justification of the practical approach to real-gas calorific values. Since no enthalpic correction is made to the ideal-gas calorific value on a volumetric basis in this calculation, the combustion reference pressure p_1 is irrelevant and is omitted from the nomenclature adopted.

8 Calculation of relative density, density and Wobbe index

8.1 Ideal gas

The relative density of the ideal gas is independent of any reference state, and is calculated from the equation

$$d^{\circ} = \sum_{j=1}^{N} x_j \times \frac{M_j}{M_{\text{air}}} \qquad \ldots (11)$$

where

d° is the relative density of the ideal gas;

M_j is the molar mass of component j;

M_{air} is the molar mass of dry air of standard composition.

Table 1 (clause 10) lists values of molar mass. Clause B.3 gives the composition of standard air; the derived value for M_{air} is 28,962 6 kg·kmol^{-1}.

The density of the ideal gas depends upon its temperature t and pressure p, and is calculated from

$$\rho^{\circ}(t,p) = \left(\frac{p}{R \cdot T}\right) \sum_{j=1}^{N} x_j \cdot M_j \qquad \ldots (12)$$

where

$\rho^{\circ}(t,p)$ is the density of the ideal gas;

R is the molar gas constant (= 8,314 510 J·mol^{-1}·K^{-1}, see clause B.1);

T (= t + 273,15) is the absolute temperature, in kelvins.

The Wobbe index of the ideal gas is calculated from the equation

$$W^{\circ}[t_1, V(t_2,p_2)] = \frac{\tilde{H}_S^{\circ}[t_1, V(t_2,p_2)]}{\sqrt{d^{\circ}}} \qquad \ldots (13)$$

where

W° is the Wobbe index of the ideal gas;

$\tilde{H}_S^{\circ}$ is calculated as described in 7.1.

8.2 Real gas

The relative density of the real gas is calculated from the equation

$$d(t,p) = \frac{d^{\circ} \cdot Z_{\text{air}}(t,p)}{Z_{\text{mix}}(t,p)} \qquad \ldots (14)$$

where

$d(t,p)$ is the relative density of the real gas;

$Z_{\text{mix}}(t,p)$ is the compression factor of the gas;

$Z_{\text{air}}(t,p)$ is the compression factor of dry air of standard composition.

The compression factor $Z_{\text{mix}}(t,p)$ is calculated from equation (3), using values of the summation factor $\sqrt{b_j}$ given for individual pure substances in table 2 (clause 10). The compression factor $Z_{\text{air}}(t,p)$ is given in clause B.3 as

Z_{air}(273,15 K, 101,325 kPa) = 0,999 41

Z_{air}(288,15 K, 101,325 kPa) = 0,999 58

Z_{air}(293,15 K, 101,325 kPa) = 0,999 63

The density of the real gas is calculated from the equation

$$\rho(t,p) = \frac{\rho^{\circ}(t,p)}{Z_{\text{mix}}(t,p)} \qquad \ldots (15)$$

where $\rho(t,p)$ is the density of the real gas.

The Wobbe index of the real gas is calculated from the equation

$$W[t_1, V(t_2,p_2)] = \frac{\tilde{H}_S[t_1, V(t_2,p_2)]}{\sqrt{d(t_2,p_2)}} \qquad \ldots (16)$$

where

W is the Wobbe index of the real gas;

$\tilde{H}_S$ is calculated as described in 7.2.

NOTE 16 Some care in the use of units is required for the calculations described in this subclause, particularly for calculations of density. With R expressed in joules per mole kelvin, p in kilopascals and M in kilograms per kilomole, the value of ρ is obtained automatically in kilograms per cubic metre, the preferred SI unit.

9 Accuracy

9.1 Precision

9.1.1 Repeatability and reproducibility

The precision of a calculated physical property value, which results solely from random errors in the analytical procedures, may be expressed in terms of repeatability and/or reproducibility, where these are defined as follows.

Repeatability: The value below which the absolute difference between a pair of successive test results obtained using the same method, on identical test material, by the same operator, using the same apparatus, in the same laboratory, within a short interval of time, may be expected to lie with a specified probability. In the absence of other indications, the probability is 95 %.

Reproducibility: The value below which the absolute difference between two single test results obtained using the same method, on identical test material, by different operators, using different apparatus, in different laboratories, may be expected to lie with a specified probability. In the absence of other indications, the probability is 95 %.

The latter quantity is usually significantly larger than the former. Each measure of the precision of a calculated physical property depends only upon the precision of the analytical data.

The general concepts of repeatability and reproducibility may be applied not only to physical properties calculated from compositional analyses, but also to each component concentration in the analyses from which the properties are derived. Consequently, the repeatability or reproducibility of a physical property value may actually be obtained in either of two apparently equivalent ways, *viz.*

a) By direct application of the above definitions to repeated calculations of the physical property in question, i.e. from the equation

$$\Delta Y = 2\sqrt{2}\left[\frac{\sum\limits_{i=1}^{n}(Y_i-\bar{Y})^2}{n-1}\right]^{1/2} \qquad \ldots (17)$$

ΔY is either the repeatability or reproducibility of Y, as appropriate;

Y_i is the value of the physical property calculated from the ith analysis of the gas;

$\bar{Y}$ is the arithmetic mean of n values of Y_i.

NOTE 17 For definitions of repeatability and reproducibility, their interpretation in terms of the standard deviation of the population of values as given by equation (17), and for the origin of the factor $2\sqrt{2}$ therein, see for example reference [26] in annex M.

b) By combining, in an appropriate manner, the repeatability or reproducibility of the concentration of each component in the gas analysis; the appropriate combination formulae are given in 9.1.2 and 9.1.3 (for the derivation of these equations, see annex H).

NOTE 18 The equivalence of a) and b) in practice as opposed to principle is open to discussion. This is because the statistical link between the methods assumes that the repeatedly measured analytical values are distributed in a Gaussian (normal) fashion for each component concentration, and that this is also the case for the set of calculated physical property values. Experience has shown that these criteria are not usually met, especially for small data sets and/or sets containing outliers.

9.1.2 Estimation of repeatability

The repeatability ΔH, at a 95 % confidence level, of the calorific value H may be calculated either from equation (17) (with Y replaced by H), or directly from the analytical data, using the appropriate expression, as follows:

a) When all components except methane are analysed, the methane (j = 1) concentration being calculated by difference, then

$$\Delta H^{\circ}_{\mathrm{mix}} = \left\{\sum_{j=2}^{N}\left[\Delta x_j \cdot (H^{\circ}_j - H^{\circ}_1)\right]^2\right\}^{1/2} \qquad \ldots (18)$$

where

$\Delta H^{\circ}_{\mathrm{mix}}$ is the repeatability of the calculated ideal-gas calorific value (molar or volumetric basis) for the mixture;

Δx_j is the repeatability of the mole fraction of component j in the mixture of N components;

H°_j is the ideal-gas calorific value of component j;

H_1^{o} is the ideal-gas calorific value of methane.

b) When all components including methane are analysed, then

$$\Delta H^{\mathrm{o}}_{\mathrm{mix}} = \left\{ \sum_{j=1}^{N} \left[\Delta x_j^{*} \cdot (H_j^{\mathrm{o}} - H^{\mathrm{o}}_{\mathrm{mix}})\right]^2 \right\}^{1/2} \qquad \ldots (19)$$

where, although $H^{\mathrm{o}}_{\mathrm{mix}}$ is calculated using the normalized mole fractions x_j, Δx_j^{*} is the repeatability of the mole fraction of component j in the mixture of N components before normalization is carried out.

The repeatability Δd of the relative density and $\Delta \rho$ of the density may be calculated from the following equations, respectively:

$$\Delta d = \frac{\Delta M}{M_{\mathrm{air}}} \qquad \ldots (20)$$

$$\Delta \rho = \frac{\Delta M \cdot p}{R \cdot T} \qquad \ldots (21)$$

where ΔM is the repeatability of the mean molar mass M of the natural gas, given by

— for case a):

$$\Delta M = \left\{ \sum_{j=2}^{N} \left[\Delta x_j \cdot (M_j - M_1)\right]^2 \right\}^{1/2} \qquad \ldots (22)$$

— For case b):

$$\Delta M = \left\{ \sum_{j=1}^{N} \left[\Delta x_j^{*} \cdot (M_j - M)\right]^2 \right\}^{1/2} \qquad \ldots (23)$$

where M_j is the molar mass of component j.

The repeatability ΔW of the Wobbe index may be calculated from the equation

$$\Delta W = W \cdot \left[\left(\frac{\Delta \tilde{H}}{\tilde{H}} \right)^2 + \left(\frac{\Delta d}{2d} \right)^2 \right]^{1/2} \qquad \ldots (24)$$

As for the calorific value, the repeatabilities ΔM, Δd, $\Delta \rho$ and ΔW may also be determined by calculation of the standard deviation of a set of calculated property values [i.e., from equation (17) with Y replaced by M, d, ρ or W, as appropriate] where the compositional analyses have been carried out in accordance with the definition of repeatability given in 9.1.1. However, the provision given in note 18 to 9.1.1 still applies.

NOTE 19 The contribution of the repeatability ΔZ of the calculated compression factor Z to the overall repeatability $\Delta \tilde{H}$ of the calorific value on a volumetric basis is small, and is therefore ignored in the above formulation; likewise, the contribution of ΔZ to the overall repeatability $\Delta \rho$ of the real-gas density, Δd of the real-gas relative density and ΔW of the real-gas Wobbe index is also ignored.

9.1.3 Estimation of reproducibility

The reproducibilities ΔH, Δd, $\Delta \rho$ and ΔW of the calorific values, relative density, density and Wobbe index may be calculated by means of the equations (18) to (24) inclusive, provided that the Δx_j and Δx_j^{*} in equations (18), (19), (22) and (23) are now identified as the appropriate reproducibilities of the mole fractions x_j. The reproducibilities may also be determined from the calculation of $2\sqrt{2}$ times the standard deviation of the population of calculated values of H, d, ρ or W, using equation (17), where the analyses of compositions have been carried out in accordance with the definition of reproducibility given in 9.1.1.

9.2 Trueness

Observations of the precision of analytical data cannot be regarded as carrying any implication for the trueness of those data; it is entirely possible to achieve excellent precision at the same time as very bad trueness.

The absolute trueness of a calculated physical property value of a natural gas mixture may be considered as resulting from the combination of three independent sources of <u>systematic error</u>, *viz.*

a) uncertainties in the basic data given in tables 1 to 5;

b) bias in the method of calculation which uses these data;

c) uncertainties (as distinct from random imprecision) in the analytical data used as input to the method.

In practice, it is difficult to make calculations of trueness due to the lack of adequate information; for example, reference back to original sources of basic data often reveals information concerning precision only (see, in this context, the discussion of methane given in annex G), and the same is often true for analytical data. In addition, a rigorous approach would provide an absolute uncertainty, whereas what is often required in practice is an estimate of the uncertainty of a physical property value relative to some datum point. For example, calorific values are often referenced to the calorific value of pure methane; consequently any uncertainty in the assumed calorific value of methane does not contribute to the relative uncertainty of the calorific value of a natural gas, or to the difference between the calorific values of two different natural gases.

Experience has shown that the relative uncertainties of the physical property values considered herein will be most strongly influenced by uncertainties in the analytical data, and that contributions from uncertainties in basic data and bias in the method of calculation will be very small. The contributions from the basic data are expected to be less than 0,05 % and from bias in the method of calculation to be less than 0,015 %. These contributions may be neglected when compared to the uncertainty in the analytical data from the analysis of a typical natural gas mixture containing 12 to 20 components.

For those cases where the contributions from uncertainties in the basic data and from bias in the method of calculation are significant when compared with the analytical uncertainty (for example, for the high accuracy analysis of mixtures of only a few components, and possibly in the future, when the accuracy of natural gas analysis has improved), a more rigorous approach, based on a), b) and c), may be necessary.

9.3 Expression of results

The number of significant figures which are given for the value of each property should reflect the expected accuracy of calculation of the property in question. Even in the case of a "perfect" analysis, the results of calculations for mixtures should be reported to no better than the following levels of significance.

Calorific value	— molar basis:	0,01 kJ·mol^{-1}
	— mass basis:	0,01 MJ·kg^{-1}
	— volumetric basis:	0,01 MJ·m^{-3}
Relative density:		0,000 1
Density:		0,000 1 kg·m^{-3}
Wobbe index:		0,01 MJ·m^{-3}

However, attention must be paid to whether the analytical data do in fact justify quoting to this level of supposed significance and, if not, the number of significant figures quoted should be reduced accordingly.

10 Tables of recommended data

Table 1 — Molar mass for components of natural gases

	Component	Values kg·kmol^{-1}
1	Methane	16,043
2	Ethane	30,070
3	Propane	44,097
4	*n*-Butane	58,123
5	2-Methylpropane	58,123
6	*n*-Pentane	72,150
7	2-Methylbutane	72,150
8	2,2-Dimethylpropane	72,150
9	*n*-Hexane	86,177
10	2-Methylpentane	86,177
11	3-Methylpentane	86,177
12	2,2-Dimethylbutane	86,177
13	2,3-Dimethylbutane	86,177
14	*n*-Heptane	100,204
15	*n*-Octane	114,231
16	*n*-Nonane	128,258
17	*n*-Decane	142,285
18	Ethylene	28,054
19	Propylene	42,081
20	1-Butene	56,108
21	*cis*-2-Butene	56,108
22	*trans*-2-Butene	56,108
23	2-Methylpropene	56,108
24	1-Pentene	70,134
25	Propadiene	40,065
26	1,2-Butadiene	54,092
27	1,3-Butadiene	54,092
28	Acetylene	26,038
29	Cyclopentane	70,134
30	Methylcyclopentane	84,161
31	Ethylcyclopentane	98,188
32	Cyclohexane	84,161
33	Methylcyclohexane	98,188
34	Ethylcyclohexane	112,215
35	Benzene	78,114
36	Toluene	92,141
37	Ethylbenzene	106,167
38	*o*-Xylene	106,167
39	Methanol	32,042
40	Methanethiol	48,109
41	Hydrogen	2,015 9
42	Water	18,015 3
43	Hydrogen sulfide	34,082
44	Ammonia	17,030 6
45	Hydrogen cyanide	27,026
46	Carbon monoxide	28,010
47	Carbonyl sulfide	60,076
48	Carbon disulfide	76,143
49	Helium	4,002 6
50	Neon	20,179 7
51	Argon	39,948
52	Nitrogen	28,013 5
53	Oxygen	31,998 8
54	Carbon dioxide	44,010
55	Sulfur dioxide	64,065
56	Dinitrogen monoxide	44,012 9
57	Krypton	83,80
58	Xenon	131,29
	Air	28,962 6

NOTE — Values of the molar mass are numerically identical to values of relative molecular mass obtained using the following relative atomic masses for the major elements involved, where the figure in brackets is the uncertainty in the last digit quoted (see reference [14] in annex M):

C	12,011 (1)
H	1,007 94 (7)
O	15,999 4 (3)
N	14,006 74 (7)
S	32,066 (6)

For compounds containing C and/or S the derived molar mass has been rounded to the third decimal place; for other compounds the fourth decimal place is given. The value for dry air of standard composition (see table B.2) is also given to four decimal places.

Table 2 — Compression factors and summation factors for components of natural gases at various metering reference conditions

All values, except for summation factors for hydrogen, helium (recalculated) and neon (estimated), are taken or inferred from reference [13] in annex M.

Component		0 °C, 101,325 kPa		15 °C, 101,325 kPa		20 °C, 101,325 kPa	
		Z	$\sqrt{b}$	Z	$\sqrt{b}$	Z	$\sqrt{b}$
1	Methane	0,997 6	0,049 0	0,998 0	0,044 7	0,998 1	0,043 6
2	Ethane	0,990 0	0,100 0	0,991 5	0,092 2	0,992 0	0,089 4
3	Propane	0,978 9	0,145 3	0,982 1	0,133 8	0,983 4	0,128 8
4	*n*-Butane	0,957 2	0,206 9	0,965 0	0,187 1	0,968 2	0,178 3
5	2-Methylpropane	0,958	0,204 9	0,968	0,178 9	0,971	0,170 3
6	*n*-Pentane	0,918	0,286 4	0,937	0,251 0	0,945	0,234 5
7	2-Methylbutane	0,937	0,251 0	0,948	0,228 0	0,953	0,216 8
8	2,2-Dimethylpropane	0,943	0,238 7	0,955	0,212 1	0,959	0,202 5
9	*n*-Hexane	0,892	0,328 6	0,913	0,295 0	0,919	0,284 6
10	2-Methylpentane	0,898	0,319 4	0,914	0,293 3	0,926	0,272 0
11	3-Methylpentane	0,898	0,319 4	0,917	0,288 1	0,928	0,268 3
12	2,2-Dimethylbutane	0,916	0,289 8	0,931	0,262 7	0,935	0,255 0
13	2,3-Dimethylbutane	0,910	0,300 0	0,925	0,273 9	0,934	0,256 9
14	*n*-Heptane	0,830	0,412 3	0,866	0,366 1	0,876	0,352 1
15	*n*-Octane	0,742	0,507 9	0,802	0,445 0	0,817	0,427 8
16	*n*-Nonane	0,613	0,622 1	0,710	0,538 5	0,735	0,514 8
17	*n*-Decane	0,434	0,752 3	0,584	0,645 0	0,623	0,614 0
18	Ethylene	0,992 5	0,086 6	0,993 6	0,080 0	0,994 0	0,077 5
19	Propylene	0,981	0,137 8	0,984	0,126 5	0,985	0,122 5
20	1-Butene	0,965	0,187 1	0,970	0,173 2	0,972	0,167 3
21	*cis*-2-Butene	0,961	0,197 5	0,967	0,181 7	0,969	0,176 1
22	*trans*-2-Butene	0,961	0,197 5	0,968	0,178 9	0,969	0,176 1
23	2-Methylpropene	0,965	0,187 1	0,971	0,170 3	0,972	0,167 3
24	1-Pentene	0,938	0,249 0	0,949	0,225 8	0,952	0,219 1
25	Propadiene	0,980	0,141 4	0,983	0,130 4	0,984	0,126 5
26	1,2-Butadiene	0,955	0,212 1	0,963	0,192 4	0,965	0,187 1
27	1,3-Butadiene	0,966	0,184 4	0,971	0,170 3	0,973	0,164 3
28	Acetylene	0,991	0,094 9	0,993	0,083 7	0,993	0,083 7
29	Cyclopentane	0,935	0,255 0	0,947	0,230 2	0,950	0,223 6
30	Methylcyclopentane	0,902	0,313 0	0,921	0,281 1	0,927	0,270 2
31	Ethylcyclopentane	0,841	0,398 7	0,876	0,352 1	0,885	0,339 1
32	Cyclohexane	0,897	0,320 9	0,918	0,286 4	0,924	0,275 7
33	Methylcyclohexane	0,855	0,380 8	0,886	0,337 6	0,894	0,325 6
34	Ethylcyclohexane	0,770	0,479 6	0,824	0,419 5	0,838	0,402 5
35	Benzene	0,909	0,301 7	0,926	0,272 0	0,936	0,253 0
36	Toluene	0,849	0,388 6	0,883	0,342 1	0,892	0,328 6
37	Ethylbenzene	0,764	0,485 8	0,823	0,420 7	0,837	0,403 7
38	*o*-Xylene	0,737	0,512 8	0,804	0,442 7	0,821	0,423 1
39	Methanol	0,773	0,476 4	0,872	0,357 8	0,892	0,328 6
40	Methanethiol	0,972	0,167 3	0,977	0,151 7	0,978	0,148 3
41	Hydrogen	1,000 6	-0,004 0	1,000 6	-0,004 8	1,000 6	-0,005 1
42	Water	0,930	0,264 6	0,945	0,234 5	0,952	0,219 1
43	Hydrogen sulfide	0,990	0,100 0	0,990	0,100 0	0,990	0,100 0
44	Ammonia	0,985	0,122 5	0,988	0,109 5	0,989	0,104 9
45	Hydrogen cyanide	0,887	0,336 2	0,912	0,296 6	0,920	0,282 8
46	Carbon monoxide	0,999 3	0,026 5	0,999 5	0,022 4	0,999 6	0,020 0
47	Carbonyl sulfide	0,985	0,122 5	0,987	0,114 0	0,988	0,109 5
48	Carbon disulfide	0,954	0,214 5	0,962	0,194 9	0,965	0,187 1
49	Helium	1,000 5	0,000 6	1,000 5	0,000 2	1,000 5	0,000 0
50	Neon	1,000 5	0,000 6	1,000 5	0,000 2	1,000 5	0,000 0
51	Argon	0,999 0	0,031 6	0,999 2	0,028 3	0,999 3	0,026 5
52	Nitrogen	0,999 5	0,022 4	0,999 7	0,017 3	0,999 7	0,017 3
53	Oxygen	0,999 0	0,031 6	0,999 2	0,028 3	0,999 3	0,026 5
54	Carbon dioxide	0,993 3	0,081 9	0,994 4	0,074 8	0,994 7	0,072 8
55	Sulfur Dioxide	0,976	0,154 9	0,979	0,144 9	0,980	0,141 4
	Air	0,999 41	—	0,999 58	—	0,999 63	—

Table 3 — Calorific values for components of natural gases at various combustion reference conditions for the ideal gas on a molar basis

All values of $\overline{H}_S^o$ (25 °C), except for methane (see annex G), are taken from reference [13] in annex M: values of $\overline{H}_S^o$ ($t_1 \neq 25$ °C) and all values of $\overline{H}_I^o$ (t_1) are obtained by a specified calculation from $\overline{H}_S^o$ (25°C) (see clause E.1).

Component		Ideal calorific value on a molar basis, $\overline{H}^\circ$ (kJ·mol^{-1})							
		25 °C		20 °C		15 °C		0 °C	
		Superior	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**
1	Methane	890,63	802,60	891,09	802,65	891,56	802,69	892,97	802,82
2	Ethane	1 560,69	1 428,64	1 561,41	1 428,74	1 562,14	1 428,84	1 564,34	1 429,12
3	Propane	2 219,17	2 043,11	2 220,13	2 043,23	2 221,10	2 043,37	2 224,01	2 043,71
4	*n*-Butane	2 877,40	2 657,32	2 878,57	2 657,45	2 879,76	2 657,60	2 883,82	2 658,45
5	2-Methylpropane	2 868,20	2 648,12	2 869,38	2 648,26	2 870,58	2 648,42	2 874,20	2 648,83
6	*n*-Pentane	3 535,77	3 271,67	3 537,17	3 271,83	3 538,60	3 272,00	3 542,89	3 272,45
7	2-Methylbutane	3 528,83	3 264,73	3 530,24	3 264,89	3 531,68	3 265,08	3 535,98	3 265,54
8	2,2-Dimethylpropane	3 514,61	3 250,51	3 516,01	3 250,67	3 517,43	3 250,83	3 521,72	3 251,28
9	*n*-Hexane	4 194,95	3 886,84	4 196,58	3 887,01	4 198,24	3 887,21	4 203,23	3 887,71
10	2-Methylpentane	4 187,32	3 879,21	4 188,95	3 879,38	4 190,62	3 879,59	4 195,61	3 880,09
11	3-Methylpentane	4 189,90	3 881,79	4 191,54	3 881,97	4 193,22	3 882,19	4 198,24	3 882,72
12	2,2-Dimethylbutane	4 177,52	3 869,41	4 179,15	3 869,59	4 180,83	3 869,80	4 185,84	3870,32
13	2,3-Dimethylbutane	4 185,28	3 877,17	4 186,93	3 877,36	4 188,60	3 877,57	4 193,63	3 878,11
14	*n*-Heptane	4 853,43	4 501,30	4 855,29	4 501,49	4 857,18	4 501,72	4 862,87	4 502,28
15	*n*-Octane	5 511,80	5 115,66	5 513,88	5 115,87	5 516,01	5 116,11	5 522,40	5 116,73
16	*n*-Nonane	6 171,15	5 730,99	6 173,46	5 731,22	6 175,82	5 731,49	6 182,91	5 732,17
17	*n*-Decane	6 829,77	6 345,59	6 832,31	6 345,85	6 834,90	6 346,14	6 842,69	6 346,88
18	Ethylene	1 411,18	1 323,15	1 411,65	1 323,20	1 412,11	1 323,24	1 413,51	1 323,36
19	Propylene	2 058,02	1 925,97	2 058,72	1 926,05	2 059,43	1 926,13	2 061,57	1 926,35
20	1-Butene	2 716,82	2 540,76	2 717,75	2 540,86	2 718,70	2 540,97	2 721,55	2 541,25
21	*cis*-2-Butene	2 710,0	2 533,9	2 711,0	2 534,1	2 711,9	2 534,2	2 714,9	2 534,6
22	*trans*-2-Butene	2 706,4	2 530,3	2 707,4	2 530,5	2 708,3	2 530,5	2 711,1	2 530,8
23	2-Methylpropene	2 700,2	2 524,1	2 701,1	2 524,2	2 702,0	2 524,3	2 704,8	2 524,5
24	1-Pentene	3 375,42	3 155,34	3 376,57	3 155,45	3 377,75	3 155,59	3 381,29	3 155,92
25	Propadiene	1 943,11	1 855,08	1 943,53	1 855,08	1 943,96	1 855,09	1 945,25	1 855,10
26	1,2-Butadiene	2 593,79	2 461,74	2 594,45	2 461,78	2 595,12	2 461,82	2 597,13	2 461,91
27	1,3-Butadiene	2 540,77	2 408,72	2 541,43	2 408,76	2 542,10	2 408,80	2 544,13	2 408,91
28	Acetylene	1 301,05	1 257,03	1 301,21	1 256,98	1 301,37	1 256,94	1 301,86	1 256,79
29	Cyclopentane	3 319,59	3 099,51	3 320,88	3 099,76	3 322,19	3 100,03	3 326,14	3 100,77
30	Methylcyclopentane	3 969,44	3 705,34	3 970,93	3 705,59	3 972,46	3 705,86	3 977,04	3 706,60
31	Ethylcyclopentane	4 628,47	4 320,36	4 630,19	4 320,63	4 631,95	4 320,92	4 637,27	4 321,75
32	Cyclohexane	3 952,96	3 688,86	3 954,47	3 689,13	3 956,02	3 689,42	3 960,67	3 690,23
33	Methylcyclohexane	4 600,64	4 292,53	4 602,35	4 292,78	4 604,09	4 293,06	4 609,34	4 293,82
34	Ethylcyclohexane	5 263,05	4 910,92	5 264,98	4 911,19	5 266,95	4 911,49	5 272,88	4 912,29
35	Benzene	3 301,43	3 169,38	3 302,15	3 169,48	3 302,86	3 169,56	3 305,03	3 169,81
36	Toluene	3 947,89	3 771,83	3 948,84	3 771,95	3 949,81	3 772,08	3 952,72	3 772,42
37	Ethylbenzene	4 607,15	4 387,07	4 608,32	4 387,20	4 609,53	4 387,37	4 613,14	4 387,77
38	*o*-Xylene	4 596,31	4 376,23	4 597,46	4 376,34	4 598,64	4 376,48	4 602,17	4 376,80
39	Methanol	764,09	676,06	764,59	676,14	765,09	676,22	766,59	676,44
40	Methanethiol	1 239,39	1 151,36	1 239,83	1 151,39	1 240,28	1 151,41	1 241,63	1 151,48
41	Hydrogen	285,83	241,81	285,99	241,76	286,15	241,72	286,63	241,56
42	Water[1)]	44,016	0	44,224	0	44,433	0	45,074	0
43	Hydrogen sulfide	562,01	517,99	562,19	517,97	562,38	517,95	562,94	517,87
44	Ammonia	382,81	316,79	383,16	316,82	383,51	316,86	384,57	316,96
45	Hydrogen cyanide	671,5	649,5	671,6	649,5	671,7	649,5	671,9	649,4
46	Carbon monoxide	282,98	282,98	282,95	282,95	282,91	282,91	282,80	282,80
47	Carbonyl sulfide	548,23	548,23	548,19	548,19	548,15	548,15	548,01	548,01
48	Carbon disulfide	1 104,49	1 104,49	1 104,41	1 104,41	1 104,32	1 104,32	1 104,06	1 104,06

1) The non-zero calorific value of water vapour is derived formally from the definition of superior calorific value, which requires condensation to the liquid state of all water vapour in the products of combustion. Thus, any water vapour present in an otherwise dry gas contributes its latent heat of vaporization to the superior calorific value of the mixture. (See annex F for a fuller explanation.)

Table 4 — Calorific values for components of natural gases at various combustion reference conditions for the ideal gas on a mass basis

All values have been obtained by dividing the appropriate $\overline{H}^\circ$ value from table 3 by the appropriate molar mass (before rounding) from table 1.

Component		Ideal calorific value on a mass basis, $\hat{H}^\circ$ (MJ·kg^{-1})							
		25 °C		20 °C		15 °C		0 °C	
		Superior	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**
1	Methane	55,516	50,029	55,545	50,032	55,574	50,035	55,662	50,043
2	Ethane	51,90	47,51	51,93	47,51	51,95	47,52	52,02	47,53
3	Propane	50,33	46,33	50,35	46,34	50,37	46,34	50,44	46,35
4	*n*-Butane	49,51	45,72	49,53	45,72	49,55	45,72	49,62	45,74
5	2-Methylpropane	49,35	45,56	49,37	45,56	49,39	45,57	49,45	45,57
6	*n*-Pentane	49,01	45,35	49,03	45,35	49,04	45,35	49,10	45,36
7	2-Methylbutane	48,91	45,25	48,93	45,25	48,95	45,25	49,01	45,26
8	2,2-Dimethylpropane	48,71	45,05	48,73	45,05	48,75	45,06	48,81	45,06
9	*n*-Hexane	48,68	45,10	48,70	45,10	48,72	45,11	48,77	45,11
10	2-Methylpentane	48,59	45,01	48,61	45,02	48,63	45,02	48,69	45,02
11	3-Methylpentane	48,62	45,04	48,64	45,05	48,66	45,05	48,72	45,06
12	2,2-Dimethylbutane	48,48	44,90	48,49	44,90	48,51	44,91	48,57	44,91
13	2,3-Dimethylbutane	48,57	44,99	48,59	44,99	48,60	45,00	48,66	45,00
14	*n*-Heptane	48,44	44,92	48,45	44,92	48,47	44,93	48,53	44,93
15	*n*-Octane	48,25	44,78	48,27	44,79	48,29	44,79	48,34	44,79
16	*n*-Nonane	48,12	44,68	48,13	44,69	48,15	44,69	48,21	44,69
17	*n*-Decane	48,00	44,60	48,02	44,60	48,04	44,60	48,09	44,61
18	Ethylene	50,30	47,16	50,32	47,17	50,34	47,17	50,39	47,17
19	Propylene	48,91	45,77	48,92	45,77	48,94	45,77	48,99	45,78
20	1-Butene	48,42	45,28	48,44	45,29	48,46	45,29	48,51	45,29
21	*cis*-2-Butene	48,30	45,16	48,32	45,16	48,33	45,17	48,39	45,17
22	*trans*-2-Butene	48,24	45,10	48,25	45,10	48,27	45,10	48,32	45,11
23	2-Methylpropene	48,13	44,99	48,14	44,99	48,16	44,99	48,21	44,99
24	1-Pentene	48,13	44,99	48,14	44,99	48,16	44,99	48,21	45,00
25	Propadiene	48,50	46,30	48,51	46,30	48,52	46,30	48,55	46,30
26	1,2-Butadiene	47,95	45,51	47,96	45,51	47,98	45,51	48,01	45,51
27	1,3-Butadiene	46,97	44,53	46,98	44,53	47,00	44,53	47,03	44,53
28	Acetylene	49,97	48,28	49,97	48,28	49,98	48,27	50,00	48,27
29	Cyclopentane	47,33	44,19	47,35	44,20	47,37	44,20	47,43	44,21
30	Methylcyclopentane	47,16	44,03	47,18	44,03	47,20	44,03	47,25	44,04
31	Ethylcyclopentane	47,14	44,00	47,16	44,00	47,17	44,01	47,23	44,01
32	Cyclohexane	46,97	43,83	46,99	43,83	47,01	43,84	47,06	43,85
33	Methylcyclohexane	46,86	43,72	46,87	43,72	46,89	43,72	46,94	43,73
34	Ethylcyclohexane	46,90	43,76	46,92	43,77	46,94	43,77	46,99	43,78
35	Benzene	42,26	40,57	42,27	40,58	42,28	40,58	42,31	40,58
36	Toluene	42,85	40,94	42,86	40,94	42,87	40,94	42,90	40,94
37	Ethylbenzene	43,40	41,32	43,41	41,32	43,42	41,33	43,45	41,33
38	*o*-Xylene	43,29	41,22	43,30	41,22	43,31	41,22	43,35	41,23
39	Methanol	23,85	21,10	23,86	21,10	23,88	21,10	23,92	21,11
40	Methanethiol	25,76	23,93	25,77	23,93	25,78	23,93	25,81	23,93
41	Hydrogen	141,79	119,95	141,87	119,93	141,95	119,91	142,19	119,83
42	Water 1)	2,44	0	2,45	0	2,47	0	2,50	0
43	Hydrogen sulfide	16,49	15,20	16,50	15,20	16,50	15,20	16,52	15,19
44	Ammonia	22,48	18,60	22,50	18,60	22,52	18,61	22,58	18,61
45	Hydrogen cyanide	24,85	24,03	24,85	24,03	24,85	24,03	24,86	24,03
46	Carbon monoxide	10,10	10,10	10,10	10,10	10,10	10,10	10,10	10,10
47	Carbonyl sulfide	9,13	9,13	9,12	9,12	9,12	9,12	9,12	9,12
48	Carbon disulfide	14,51	14,51	14,50	14,50	14,50	14,50	14,50	14,50

1) The non-zero calorific value of water vapour is derived formally from the definition of superior calorific value, which requires condensation to the liquid state of all water vapour in the products of combustion. Thus, any water vapour present in an otherwise dry gas contributes its latent heat of vaporization to the superior calorific value of the mixture. (See annex F for a fuller explanation.)

Table 5 — Calorific values for components of natural gases at various combustion and metering reference conditions for the ideal gas on a volumetric basis.

All values have been obtained by multiplying the appropriate $\overline{H}^\circ$ value from table 3 by $p_2/R \cdot T_2$.

	Component	Ideal calorific value on a volumetric basis $\tilde{H}^\circ$ (MJ·m^{-3})											
		15/15 °C		0/0 °C		15/0 °C		25/0 °C		20/20 °C		25/20 °C	
		Superior	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**	**Superior**	**Inferior**
1	Methane	37,706	33,948	39,840	35,818	39,777	35,812	39,735	35,808	37,044	33,367	37,024	33,365
2	Ethane	66,07	60,43	69,79	63,76	69,69	63,75	69,63	63,74	64,91	59,39	64,88	59,39
3	Propane	93,94	86,42	99,22	91,18	99,09	91,16	99,01	91,15	92,29	84,94	95,25	84,93
4	*n*-Butane	121,79	112,40	128,66	118,61	128,48	118,57	128,37	118,56	119,66	110,47	119,62	110,47
5	2-Methylpropane	121,40	112,01	128,23	118,18	128,07	118,16	127,96	118,15	119,28	110,09	119,23	110,08
6	*n*-Pentane	149,66	138,38	158,07	146,00	157,87	145,98	157,75	145,96	147,04	136,01	146,99	136,01
7	2-Methylbutane	149,36	138,09	157,76	145,69	157,57	145,67	157,44	145,66	146,76	135,72	146,70	135,72
8	2,2-Dimethylpropane	148,76	137,49	157,12	145,06	156,93	145,04	156,80	145,02	146,16	135,13	146,11	135,13
9	*n*-Hexane	177,55	164,40	187,53	173,45	187,30	173,43	187,16	173,41	174,46	161,59	174,39	161,58
10	2-Methylpentane	177,23	164,08	187,19	173,11	186,96	173,09	186,82	173,07	174,14	161,27	174,07	161,26
11	3-Methylpentane	177,34	164,19	187,30	173,23	187,08	173,20	186,93	173,19	174,25	161,38	174,18	161,37
12	2,2-Dimethylbutane	176,82	163,66	186,75	172,67	186,53	172,65	186,38	172,63	173,73	160,86	173,66	160,86
13	2,3-Dimethylbutane	177,15	163,99	187,10	173,02	186,87	173,00	186,73	172,98	174,05	161,19	173,99	161,18
14	*n*-Heptane	205,42	190,39	216,96	200,87	216,70	200,84	216,53	200,82	201,84	187,13	201,76	187,12
15	*n*-Octane	233,28	216,37	246,38	228,28	246,10	228,25	245,91	228,23	229,22	212,67	229,13	212,66
16	*n*-Nonane	261,19	242,40	275,85	255,74	275,53	255,71	275,32	255,69	256,64	238,25	256,54	238,24
17	*n*-Decane	289,06	268,39	305,29	283,16	304,94	283,13	304,71	283,11	284,03	263,80	283,92	263,79
18	Ethylene	59,72	55,96	63,06	59,04	63,00	59,04	62,96	59,03	58,68	55,01	58,66	55,00
19	Propylene	87,10	81,46	91,98	85,94	91,88	85,93	91,82	85,93	85,58	80,07	85,55	80,06
20	1-Butene	114,98	107,46	121,42	113,38	121,29	113,36	121,21	113,36	112,98	105,63	112,94	105,62
21	*cis*-2-Butene	114,69	107,18	121,12	113,08	120,99	113,06	120,91	113,05	112,70	105,34	112,66	105,34
22	*trans*-2-Butene	114,54	107,02	120,96	112,91	120,83	112,90	120,75	112,89	112,55	105,19	112,51	105,19
23	2-Methylpropene	114,27	106,76	120,67	112,63	120,55	112,62	120,47	112,61	112,29	104,93	112,25	104,93
24	1-Pentene	142,85	133,46	150,86	140,80	150,70	140,79	150,59	140,77	140,37	131,18	140,32	131,17
25	Propadiene	82,21	78,46	86,79	82,76	86,73	82,76	86,69	82,76	80,79	77,12	80,78	77,12
26	1,2-Butadiene	109,75	104,12	115,87	109,84	115,78	109,83	115,72	109,83	107,85	102,34	107,83	102,34
27	1,3-Butadiene	107,51	101,87	113,51	107,47	113,42	107,47	113,36	107,46	105,65	100,13	105,62	100,13
28	Acetylene	55,04	53,16	58,08	56,07	58,06	56,08	58,05	56,08	54,09	52,25	54,09	52,26
29	Cyclopentane	140,50	131,11	148,40	138,34	148,22	138,31	148,10	138,28	138,05	128,86	138,00	128,85
30	Methylcyclopentane	168,00	156,73	177,43	165,37	177,23	165,34	177,10	165,31	165,08	154,04	165,01	154,03
31	Ethylcyclopentane	195,90	182,74	206,89	192,81	206,65	192,78	206,50	192,75	192,48	179,61	192,41	179,60
32	Cyclohexane	167,31	156,03	176,70	164,64	176,50	164,60	176,36	164,58	164,39	153,36	164,33	153,35
33	Methylcyclohexane	194,72	181,56	205,64	191,57	205,41	191,53	205,26	191,51	191,32	178,45	191,25	178,44
34	Ethylcyclohexane	222,75	207,72	235,25	219,16	234,98	219,13	234,81	219,10	218,87	204,16	218,79	204,15
35	Benzene	139,69	134,05	147,45	141,42	147,36	141,41	147,29	141,40	137,27	131,76	137,24	131,75
36	Toluene	167,05	159,53	176,35	168,31	176,22	168,29	176,13	168,28	164,16	156,80	164,12	156,80
37	Ethylbenzene	194,95	185,55	205,81	195,76	205,65	195,74	205,55	195,73	191,57	182,38	191,52	182,37
38	*o*-Xylene	194,49	185,09	205,32	195,27	205,17	195,26	205,06	195,24	191,12	181,93	191,07	181,92
39	Methanol	32,36	28,60	34,20	30,18	34,13	30,17	34,09	30,16	31,78	28,11	31,76	28,10
40	Methanethiol	52,45	48,70	55,40	51,37	55,33	51,37	55,30	51,37	51,54	47,86	51,52	47,86
41	Hydrogen	12,102	10,223	12,788	10,777	12,767	10,784	12,752	10,788	11,889	10,050	11,882	10,052
42	Water[1]	1,88	0	2,01	0	1,98	0	1,96	0	1,84	0	1,83	0
43	Hydrogen sulfide	23,78	21,91	25,12	23,10	25,09	23,11	25,07	23,11	23,37	21,53	23,36	21,53
44	Ammonia	16,22	13,40	17,16	14,14	17,11	14,14	17,08	14,13	15,93	13,17	15,91	13,17
45	Hydrogen cyanide	28,41	27,47	29,98	28,97	29,97	28,98	29,96	28,98	27,92	27,00	27,91	27,00
46	Carbon monoxide	11,96	11,96	12,62	12,62	12,62	12,62	12,63	12,63	11,76	11,76	11,76	11,76
47	Carbonyl sulfide	23,18	23,18	24,45	24,45	24,46	24,46	24,46	24,46	22,79	22,79	22,79	22,79
48	Carbon disulfide	46,70	46,70	49,26	49,26	49,27	49,27	49,28	49,28	45,91	45,91	45,91	45,91

NOTES

1 The reference pressure for both combustion and metering is 101,325 kPa in all cases.

2 The column headings "t_1/t_2 °C" refer to the reference temperatures for combustion and metering, respectively.

[1] The non-zero calorific value of water vapour is derived formally from the definition of superior calorific value, which requires condensation to the liquid state of all water vapour in the products of combustion. Thus, any water vapour present in an otherwise dry gas contributes its latent heat of vaporization to the superior calorific value of the mixture. (See annex F for a fuller explanation.)

Annex A
(normative)

Symbols and units

Symbol	Meaning	Unit
a, b, c, d, e	Atomic indices for the generalized molecular species $C_aH_bO_cN_dS_e$	—
b	Gas law deviation coefficient ($b = 1 - Z$)	—
$\sqrt{b}$	Summation factor	—
B	Second virial coefficient	$m^3 \cdot mol^{-1}$
C	Third virial coefficient	$m^6 \cdot mol^{-2}$
c_p	Molar isobaric heat capacity	$J \cdot mol^{-1} \cdot K^{-1}$
d	Relative density	—
h	Molar enthalpy	$J \cdot mol^{-1}$
$\overline{H}$	Calorific value on a molar basis	$kJ \cdot mol^{-1}$
$\hat{H}$	Calorific value on a mass basis	$MJ \cdot kg^{-1}$
$\tilde{H}$	Calorific value on a volumetric basis	$MJ \cdot m^{-3}$
K	$\sum_{j=1}^{N}(x_j^{*})$	—
L	molar enthalpy of vaporization of water	$kJ \cdot mol^{-1}$
M	Molar mass	$kg \cdot kmol^{-1}$
n	Number of determinations in a set of values	—
N	Number of components in a mixture	—
p	Pressure (absolute)	kPa
Q	qth virial coefficient	$m^{3(q-1)} \cdot mol^{-(q-1)}$
R	Molar gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
t	Celsius temperature	°C
T	Thermodynamic (absolute) temperature	K
V	Volume	m^3
W	Wobbe index	$MJ \cdot m^{-3}$
x	Mole fraction	—
y	Volume fraction	—
Y	General (unspecified) physical property	—
Z	Compression factor	—
ρ	Density	$kg \cdot m^{-3}$
ν	Stoichiometric coefficient	—
ω	Acentric factor	—

Subscripts

c	Value at the gas-liquid critical point
i	Identifier of a particular value in a set
I	Inferior (calorific value)
j	Component identifier
k	Component identifier
m	Quantity per mole
r	Quantity divided by its value at the critical point
s	At saturation
S	Superior (calorific value)
w	For water vapour
air	For air
mix	For the mixture
1	Combustion reference state
2	Metering reference state

Superscripts

$^{\circ}$	For the ideal gas state
$*$	Non-normalized value

Prefix

Δ	Denotes the repeatability or reproducibility of the physical property prefixed

Annex B
(normative)

Values of auxiliary constants, etc.

B.1 Molar gas constant

The current recommended value of the molar gas constant R is given in reference [15] in annex M:

$$R = (8{,}314\ 510 \pm 0{,}000\ 070)\ \text{J·mol}^{-1}\text{·K}^{-1} \quad \ldots (\text{B.1})$$

B.2 Critical constants and acentric factors

Selected values for the critical temperature T_c, the critical pressure p_c and the acentric factor ω, which have been used in the derivation of many of the compression factor values Z given in table 2 by means of the Pitzer-Curl equation (see E.2), are given in table B.1. The source of all values is reference [13] in annex M.

B.3 Properties of dry air

The recommended molar composition of dry air is given in table B.2. This is collated from the work of Jones[16] and Giacomo[17], and is as given in reference [13]. Note that many alternative sources, including ISO 2533[1] give the volumetric composition rather than the molar composition; the latter is more appropriate for the direct calculation of mean molar mass (molecular weight).

The resulting value for the molar mass of dry air rounded to the fourth decimal place is

$$M_{\text{air}} = 28{,}962\ 6\ \text{kg·kmol}^{-1} \quad \ldots (\text{B.2})$$

The value of the compression factor of dry air of standard composition at each of the three commonly used metering reference conditions should be taken[13] as

$$Z_{\text{air}}(273{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 0{,}999\ 41 \quad \ldots (\text{B.3})$$

$$Z_{\text{air}}(288{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 0{,}999\ 58 \quad \ldots (\text{B.4})$$

$$Z_{\text{air}}(293{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 0{,}999\ 63 \quad \ldots (\text{B.5})$$

The real-gas density of air of standard composition to which these values give rise are

$$\rho_{\text{air}}(273{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 1{,}292\ 923\ \text{kg·m}^{-3} \quad \ldots (\text{B.6})$$

$$\rho_{\text{air}}(288{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 1{,}225\ 410\ \text{kg·m}^{-3} \quad \ldots (\text{B.7})$$

$$\rho_{\text{air}}(293{,}15\ \text{K},\ 101{,}325\ \text{kPa}) = 1{,}204\ 449\ \text{kg·m}^{-3} \quad \ldots (\text{B.8})$$

B.4 Enthalpy of vaporization of water

The standard molar enthalpy of vaporization of water is required at each of the four commonly used combustion reference conditions, in order to facilitate calculations of the difference between the ideal-gas superior calorific value and the ideal-gas inferior calorific value (molar basis) for each component. The following values[13] have been used in the derivation of the inferior calorific values given in table 3.

$$L^{\circ}(273{,}15\ \text{K}) = 45{,}074\ \text{kJ·mol}^{-1} \quad \ldots (\text{B.9})$$

$$L^{\circ}(288{,}15\ \text{K}) = 44{,}433\ \text{kJ·mol}^{-1} \quad \ldots (\text{B.10})$$

$$L^{\circ}(293{,}15\ \text{K}) = 44{,}224\ \text{kJ·mol}^{-1} \quad \ldots (\text{B.11})$$

$$L^{\circ}(298{,}15\ \text{K}) = 44{,}016\ \text{kJ·mol}^{-1} \quad \ldots (\text{B.12})$$

Table B.1 — Critical properties

Component		Critical temperature K	Critical pressure kPa	Acentric factor
1	Methane	190,555	4 598,8	0,011 5
2	Ethane	305,83	4 880	0,090 8
3	Propane	369,82	4 250	0,145 4
4	*n*-Butane	425,14	3 784	0,192 8
5	2-Methylpropane	408,13	3 648	0,175 6
6	*n*-Pentane	469,69	3 364	0,251 0
7	2-Methylbutane	460,39	3 381	0,227 3
8	2,2-Dimethylpropane	433,75	3 199	0,197 0
9	*n*-Hexane	506,4	3 030	0,295 7
10	2-Methylpentane	497,5	3 010	0,279 1
11	3-Methylpentane	504,4	3 120	0,275 0
12	2,2-Dimethylbutane	488,7	3 080	0,231 0
13	2,3-Dimethylbutane	499,9	3 130	0,247 3
14	*n*-Heptane	539,2	2 740	0,350 6
15	*n*-Octane	568,4	2 490	0,394 2
16	*n*-Nonane	594,4	2 280	0,443 7
17	*n*-Decane	617,8	2 090	0,490 2
18	Ethylene	282,35	5 042	0,085 6
19	Propylene	364,85	4 601	0,147 7
20	1-Butene	419,53	4 023	0,187 4
21	*cis*-2-Butene	435,58	4 220	0,204 4
22	*trans*-2-Butene	428,63	4 050	0,213 8
23	2-Methylpropene	417,90	4 000	0,189 8
24	1-Pentene	464,78	3 526	0,245 0
25	Propadiene	393	5 470	0,149
26	1,2-Butadiene	443,7	4 500	0,339 4
27	1,3-Butadiene	425	4 330	0,181 4
28	Acetylene	308,33	6 139	0,184 1
29	Cyclopentane	511,61	4 502	0,192 3
30	Methylcyclopentane	532,73	3 784	0,239 5
31	Ethylcyclopentane	569,46	3 397	0,282 6
32	Cyclohexane	553,5	4 074	0,214 4
33	Methylcyclohexane	572,12	3 471	0,233 3
34	Ethylcyclohexane	609	3 040	0,242 6
35	Benzene	562,16	4 898	0,210 0
36	Toluene	591,80	4 106	0,256 6
37	Ethylbenzene	617,20	3 606	0,301 1
38	*o*-Xylene	630,33	3 734	0,313 6
39	Methanol	512,64	8 092	0,556
40	Methanethiol	470,0	7 230	0,153
41	Hydrogen	33,2	1 297	− 0,218
42	Water	647,14	22 064	0,328
43	Hydrogen sulfide	373,2	8 940	0,109
44	Ammonia	405,5	11 350	0,250
45	Hydrogen cyanide	456,7	5 390	0,388
46	Carbon monoxide	132,85	3 494	0,053
47	Carbonyl sulfide	378,8	6 349	0,096
48	Carbon disulfide	552	7 900	0,109
49	Helium	5,19	227	− 0,365
50	Neon	44,40	2 760	− 0,029
51	Argon	150,65	4 866	0,001
52	Nitrogen	126,2	3 390	0,039
53	Oxygen	154,58	5 043	0,025
54	Carbon dioxide	304,20	7 386	0,239
55	Sulfur dioxide	430,8	7 884	0,256

Table B.2 — Molar composition of dry air

Species	Mole fraction
Nitrogen	0,781 02
Oxygen	0,209 46
Argon	0,009 16
Carbon dioxide	0,000 33
Neon	0,000 018 2
Helium	0,000 005 2
Methane	0,000 001 5
Krypton	0,000 001 1
Hydrogen	0,000 000 5
Dinitrogen monoxide	0,000 000 3
Carbon monoxide	0,000 000 2
Xenon	0,000 000 1

Annex C
(informative)

Conversion of volume fractions to mole fractions

If the composition is known in volume fractions at the metering reference conditions (t_2,p_2), the conversion to mole fractions may be carried out using the equation

$$x_j = \frac{\dfrac{y_j}{Z_j(t_2,p_2)}}{\sum_{j=1}^{N}\left[\dfrac{y_j}{Z_j(t_2,p_2)}\right]} \qquad \text{. . . (C.1)}$$

for all j.

Annex D
(informative)

Examples of calculations

Table D.1 gives calculations, presented in a simple spreadsheet style, of the relative molecular mass, the superior ideal molar calorific value and the compression factor of a natural gas of a given composition, from basic physical property data, for the "15/15 °C" reference conditions (ISO standard reference conditions). For the purposes of these example calculations, numerical values of all quantities used have been rounded to the fifth significant digit, and used as such in any subsequent calculations. In reality, all calculations should be performed using the full number of digits available on the calculator or computer, and only rounded at the final line to the correctly reported number of digits (see 9.3). According to the methods described in this International Standard, the various other physical properties of the natural gas are calculated as follows.

NOTE 20 The entire calculation procedure for the calorific value given in this annex is for the superior calorific value only. Calculations of the inferior calorific value are entirely analogous.

D.1 Calorific value on a molar basis
(clause 5)

From table D.1, the superior calorific value on a molar basis, $\overline{H}^{\circ}_{\mathrm{S}}$, of the ideal gas at 15 °C is, after rounding, 919,09 kJ·mol^{-1}.

This is also taken as the value of $\overline{H}_{\mathrm{S}}$, the calorific value of the real gas, the enthalpic correction from ideal to real gas being small enough to neglect (see note 13 to 5.2).

D.2 Calorific value on a mass basis
(clause 6)

In accordance with clause 6, the superior calorific value on a mass basis, $\hat{H}^{\circ}_{\mathrm{S}}$, of the ideal gas is calculated from equation (5):

$$\hat{H}^{\circ}_{\mathrm{S}}(t_1) = \frac{\overline{H}^{\circ}_{\mathrm{S}}(t_1)}{M} \qquad \ldots \text{(D.1)}$$

where, from table D.1,

$\overline{H}^{\circ}_{\mathrm{S}}$(15 °C) is 919,09 kJ·mol^{-1};

M is 17,478 kg·kmol^{-1}.

Thus

$$\hat{H}^{\circ}_{\mathrm{S}}(15\ ^{\circ}\mathrm{C}) = \frac{919{,}09}{17{,}478}$$

$$= 52{,}586\ \mathrm{MJ{\cdot}kg^{-1}},$$

reported as 52,59 MJ·kg^{-1}.

Alternatively, $\hat{H}^{\circ}_{\mathrm{S}}$ can be calculated from equation (7)

$$\hat{H}^{\circ}_{\mathrm{S}}(t_1) = \sum_{j=1}^{N}\left(x_j \times \frac{\hat{M}_j}{M}\right)\left(\hat{H}^{\circ}_{\mathrm{S}}\right)_j(t_1) \qquad \ldots \text{(D.2)}$$

This calculation also gives a calorific value of 52,59 MJ·kg^{-1}.

D.3 Calorific value on a volumetric basis
(clause 7)

In accordance with 7.1, the superior calorific value on a volumetric basis, $\tilde{H}^{\circ}_{\mathrm{S}}$, of the ideal gas is calculated from equation (8):

$$\tilde{H}^{\circ}_{\mathrm{S}}[t_1, V(t_2, p_2)] = \overline{H}^{\circ}_{\mathrm{S}}(t_1) \times \frac{p_2}{R \cdot T_2} \qquad \ldots \text{(D.3)}$$

where from table D.1,

$\overline{H}^{\circ}_{\mathrm{S}}$(15 °C) is 919,09 kJ·mol^{-1};

p_2 is 101,325 kPa;

T_2 is 288,15 K;

R, the molar gas constant, is 8,314 510 J·mol^{-1}·K^{-1}.

Thus

$$\tilde{H}^{\circ}_{\mathrm{S}}[15\ ^{\circ}\mathrm{C}, V(15\ ^{\circ}\mathrm{C}, 101{,}325\ \mathrm{kPa})]$$

$$= \frac{919{,}09 \times 101{,}325}{8{,}314\ 510 \times 288{,}15}$$

= 38,870 MJ·m^{-3}, reported as 38,87 MJ·m^{-3}.

Alternatively, $\tilde{H}_S^o$ can be calculated from equation (9):

$$\tilde{H}_S^o[t_1, V(t_2,p_2)] = \sum_{j=1}^{N} x_j \cdot \tilde{H}_j^o[t_1, V(t_2,p_2)] \qquad \ldots (D.4)$$

which also gives a value of 38,87 MJ·m^{-3}.

The effect of the change from ideal to real gas is calculated in accordance with the procedure described in 7.2

$$\tilde{H}_S[t_1, V(t_2,p_2)] = \frac{\tilde{H}_S^o[t_1, V(t_2,p_2)]}{Z_{mix}(t_2,p_2)} \qquad \ldots (D.5)$$

where Z_{mix}, the compression factor of the gas mixture, is calculated from equation (3):

$$Z_{mix}(t_2,p_2) = 1 - \left[\sum_{j=1}^{N} x_j \cdot \sqrt{b_j}\right]^2 \qquad \ldots (D.6)$$

From table D.1, the value of the sum of the mole fraction summation factors is 0,047 85; hence

$$Z_{mix}(15\ °C, 101{,}325\ kPa) = 1 - (0{,}047\ 85)^2$$

$$= 0{,}997\ 71, \text{ reported as } 0{,}997\ 7$$

and the superior calorific value of the real gas is

$$\tilde{H}_S[15\ °C, V(15\ °C, 101{,}325\ kPa)]$$

$$= \frac{38{,}87}{0{,}997\ 71}$$

$$= 38{,}959\ MJ \cdot m^{-3}, \text{ reported as } 38{,}96\ MJ \cdot m^{-3}.$$

D.4 Relative density, density and Wobbe index (clause 8)

D.4.1 Relative density

In accordance with 8.1, the relative density of the ideal gas is calculated from equation (11):

$$d^o = \sum_{j=1}^{N} x_j \times \frac{M_j}{M_{air}} \qquad \ldots (D.7)$$

Using the data from table D.1 and the value for M_{air} of 28,962 6 kg·kmol^{-1}, we obtain

$$d^o = \frac{17{,}478}{28{,}962\ 6}$$

$$= 0{,}603\ 47, \text{ reported as } 0{,}603\ 5.$$

In accordance with 8.2, the relative density of the real gas is calculated from equation (14):

$$d(t_2,p_2) = \frac{d^o \cdot Z_{air}(t_2,p_2)}{Z_{mix}(t_2,p_2)} \qquad \ldots (D.8)$$

where

Z_{air} (15 °C, 101,325 kPa) is 0,999 58 (see table 2);

Z_{mix} is 0,997 71 (see clause D.3).

Thus

$$d(15\ °C, 101{,}325\ kPa)$$

$$= \frac{0{,}603\ 47 \times 0{,}999\ 58}{0{,}997\ 71}$$

$$= 0{,}604\ 60, \text{ reported as } 0{,}604\ 6.$$

D.4.2 Density

In accordance with 8.1, the density of the ideal gas is calculated from equation (12):

$$\rho^o(t_2,p_2) = \frac{p_2}{R \cdot T_2} \sum_{j=1}^{N} x_j \cdot M_j \qquad \ldots (D.9)$$

Thus

$$\rho^o(15\ °C, 101{,}325\ kPa) = \frac{17{,}478 \times 101{,}325}{8{,}314\ 510 \times 288{,}15}$$

$$= 0{,}739\ 18\ kg \cdot m^{-3}, \text{ reported as } 0{,}739\ 2\ kg \cdot m^{-3}.$$

From 8.2, the density of the real gas is given by equation (15):

$$\rho(t_2,p_2) = \frac{\rho^o(t_2,p_2)}{Z_{mix}(t_2,p_2)}$$

Thus

$$\rho(15\ °C, 101{,}325\ kPa) = \frac{0{,}739\ 18}{0{,}997\ 71}$$

$$= 0{,}740\ 88\ kg \cdot m^{-3}, \text{ reported as } 0{,}740\ 9\ kg \cdot m^{-3}.$$

D.4.3 Wobbe index

In accordance with 8.1, the Wobbe index of the ideal gas is calculated from equation (13):

$$W^o[t_1, V(t_2,p_2)] = \frac{\tilde{H}_S^o[t_1, V(t_2,p_2)]}{\sqrt{d^o}} \qquad \ldots (D.10)$$

Thus

$$W^o[15\ °C, V(15\ °C, 101{,}325\ kPa)] = \frac{38{,}870}{\sqrt{0{,}603\ 47}}$$

$$= 50{,}036\ \mathrm{MJ\cdot m^{-3}},\ \text{reported as } 50{,}04\ \mathrm{MJ\cdot m^{-3}}.$$

From 8.2, the Wobbe index of the real gas is given by equation (16):

$$W[t_1, V(t_2, p_2)] = \frac{\tilde{H}_S[t_1, V(t_2, p_2)]}{\sqrt{d(t_2, p_2)}} \qquad \text{. . . (D.11)}$$

Thus

$$W[15\ °\mathrm{C}, V(15\ °\mathrm{C}, 101{,}325\ \mathrm{kPa})] = \frac{38{,}959}{\sqrt{0{,}604\ 6}}$$

$$= 50{,}104\ \mathrm{MJ\cdot m^{-3}},\ \text{reported as } 50{,}10\ \mathrm{MJ\cdot m^{-3}}$$

Note that all the figures calculated in this annex are identical to those given by the computer program described in annex K, except that for W. However, if the full number of digits is carried throughout the example calculations leading to the value for W, then a correct figure of 50,11 MJ·m^{-3} results, as in annex K.

D.5 Precision (clause 9)

Table D.2 gives repeatability calculations, presented in a format similar to that of table D.1, for the same gas mixture. Only the case where methane is analysed (rather than calculated by difference) is considered. In order to perform these calculations, values need to be known for the repeatability, using non-normalized mole fraction data, of each individual component. The values used are given in the fifth column of table D.2.

D.5.1 Repeatability of calorific value on a molar basis

From table D.2, the repeatability $\Delta\overline{H}^{\mathrm{o}}_{\mathrm{mix}}$ of the ideal-gas superior calorific value of 919,09 kJ·mol^{-1} is ± 0,11 kJ·mol^{-1} [see equation (19)].

D.5.2 Repeatability of calorific value on a mass basis

To obtain the repeatability for the ideal gas on a mass basis, the repeatability on a molar basis is divided by the molar mass value for the gas of 17,478 kg·kmol^{-1}.

$$\Delta\hat{H}^{\mathrm{o}}_{\mathrm{mix}} = \frac{0{,}11}{17{,}478}$$

$$= 0{,}006\ \mathrm{MJ\cdot kg^{-1}},\ \text{reported as } \pm\ 0{,}01\ \mathrm{MJ\cdot kg^{-1}}.$$

The repeatability of the superior calorific value on a mass basis of 52,59 MJ·kg^{-1} is ± 0,01 MJ·kg^{-1}.

D.5.3 Repeatability of calorific value on a volumetric basis

To obtain the repeatability for the ideal gas on a volumetric basis, the repeatability on a molar basis is multiplied by $p_2/R\cdot T_2$.

$$\Delta\tilde{H}^{\mathrm{o}}_{\mathrm{mix}} = \frac{0{,}11 \times 101{,}325}{8{,}314\ 510 \times 288{,}15}$$

$$= 0{,}005\ \mathrm{MJ\cdot m^{-3}},\ \text{reported as } \pm\ 0{,}01\ \mathrm{MJ\cdot m^{-3}}.$$

The repeatability on the ideal-gas superior calorific value on a volumetric basis of 38,87 MJ·m^{-3} is ± 0,01 MJ·m^{-3}.

D.5.4 Repeatability of relative density, density and Wobbe Index

D.5.4.1 Relative density

The repeatability of the relative density (either ideal or real) is calculated from equation (20):

$$\Delta d = \frac{\Delta M}{M_{\mathrm{air}}}$$

where

ΔM, from table D.2 [see equation (23)], is ± 0,003 1 kg·kmol^{-1};

M_{air} is 28,962 6 kg·kmol^{-1}.

Thus

$$\Delta d = \frac{0{,}003\ 1}{28{,}962\ 6}$$

$$= 0{,}000\ 11,\ \text{reported as } \pm\ 0{,}000\ 1.$$

The repeatability on the ideal relative density of 0,603 5 and on the real relative density of 0,604 6 is ± 0,000 1.

D.5.4.2 Density

The repeatability of the density (either ideal or real) is calculated from equation (21):

$$\Delta\rho = \frac{\Delta M\cdot p}{R\cdot T}$$

$$= \frac{0{,}003\ 1 \times 101{,}325}{8{,}314\ 510 \times 288{,}15}$$

$$= 0{,}000\ 13\ \text{reported as } \pm\ 0{,}000\ 1\ \mathrm{kg\cdot m^{-3}}.$$

The repeatability on the ideal density of 0,739 2 kg·m^{-3} and on the real density of 0,740 9 kg·m^{-3} is ± 0,000 1 kg·m^{-3}.

D.5.4.3 Wobbe index

The repeatability of the ideal Wobbe index is calculated from equation (24):

$$\Delta W^{\circ} = W^{\circ} \cdot \left[\left(\frac{\Delta \tilde{H}^{\circ}}{\tilde{H}^{\circ}} \right)^2 + \left(\frac{\Delta d^{\circ}}{2 d^{\circ}} \right)^2 \right]^{1/2}$$

$$= 50{,}04 \left[\left(\frac{0{,}01}{38{,}87} \right)^2 + \left(\frac{0{,}000\ 1}{2 \times 0{,}603\ 5} \right)^2 \right]^{1/2}$$

$= 0{,}001\ 3$ MJ·m^{-3}, reported as ± 0,01 MJ·m^{-3}.

The repeatability on the ideal Wobbe Index of 50,04 MJ·m^{-3} is ± 0,01 MJ·m^{-3}.

Table D.1 — Details of an example of a property calculation

Component j	**Molar mass** M_j kg·kmol^{-1}	**Superior calorific value** $(\overline{H}_S^{\circ})_j$(15 °C) kJ·mol^{-1}	**Summation factor** $\sqrt{b_j}$ (15 °C, 101,325 kPa)	**Mole fraction** x_j	**Mole fraction × molar mass per mole** $x_j \cdot M_j$ kg·kmol^{-1}	**Mole fraction × calorific value** $x_j \cdot (\overline{H}_S^{\circ})_j$ kJ·mol^{-1}	**Mole fraction × summation factor** $\delta x_j \cdot \sqrt{b_j}$
Methane	16,043	891,56	0,044 7	0,924 7	14,835 0	824,43	0,041 33
Ethane	30,070	1 562,14	0,092 2	0,035 0	1,052 5	54,67	0,003 23
Propane	44,097	2 221,10	0,133 8	0,009 8	0,432 2	21,77	0,001 31
n-Butane	58,123	2 879,76	0,187 1	0,002 2	0,127 9	6,34	0,000 41
2-Methylpropane	58,123	2 870,58	0,178 9	0,003 4	0,197 6	9,76	0,000 61
n-Pentane	72,150	3 538,60	0,251 0	0,000 6	0,043 3	2,12	0,000 15
Nitrogen	28,013 5	0	0,017 3	0,017 5	0,490 2	0	0,000 30
Carbon dioxide	44,010	0	0,074 8	0,006 8	0,299 3	0	0,000 51
Totals				1,000 0	17,478	919,09	0,047 85

Table D.2 — Details of an example of a precision calculation

Component j	**Molar mass** M_j kg·kmol^{-1}	**Superior calorific value** $(\overline{H}_S^{\circ})_j$(15 °C) kJ·mol^{-1}	**Mole fraction** x_j	**Repeatability on non-normalized mole fraction** Δx_j^*	$\{\Delta x_j^* \cdot [(\overline{H}_S^{\circ})_j - (\overline{H}_S^{\circ})_{\text{mix}}]\}^2$	$[\Delta x_j^* \cdot (M_j - M)]^2$
Methane	16,043	891,56	0,924 7	0,001 532	0,001 779	0,000 004 83
Ethane	30,070	1 562,14	0,035 0	0,000 086	0,003 058	0,000 001 17
Propane	44,097	2 221,10	0,009 8	0,000 032	0,001 736	0,000 000 73
n-Butane	58,123	2 879,76	0,002 2	0,000 010	0,000 384	0,000 000 17
2-Methylpropane	58,123	2 870,58	0,003 4	0,000 006	0,000 137	0,000 000 06
n-Pentane	72,150	3 538,60	0,000 6	0,000 004	0,000 110	0,000 000 05
Nitrogen	28,013 5	0	0,017 50	0,000 064	0,003 460	0,000 000 45
Carbon dioxide	44,010	0	0,006 8	0,000 052	0,002 284	0,000 001 90
Totals			1,000 0		0,012 948	0,000 009 36
Square roots of totals					0,113 8	0,003 06

Annex E
(informative)

Behaviour of ideal and real gases

E.1 Variation of ideal-gas enthalpy of combustion with temperature

In 4.1, reference is made to the fact that the ideal-gas (standard) enthalpy of combustion $-\overline{H}^{\circ}_{S}$ of any gas or gas mixture varies in accordance with the temperature at which combustion is deemed to take place (i.e. the combustion reference temperature). The variation observed, although relatively small in magnitude, is significant and must not be ignored. However, the variation is generally complex, and in consequence it is not practicable to provide formulations which would enable the user to determine $\overline{H}^{\circ}_{S}$ at any arbitrary combustion reference temperature. Instead, values of $\overline{H}^{\circ}_{S}$ for each distinct chemical component listed in this International Standard are given in table 3 for each of the commonly used combustion reference temperatures of 298,15 K, 293,15 K, 288,15 K and 273,15 K (25 °C, 20 °C, 15 °C and 0 °C, respectively).

The values listed have been derived as follows. Consider the generalized combustion reaction for the pure, supposedly gaseous, chemical component ($C_aH_bO_cN_dS_e$) in which the atomic indices a to e are non-negative integers (including zero) whose values define the specific component in question (e.g. for $a = 1$, $b = 4$, $c = d = e = 0$, the species is CH_4), *viz.*

$$C_aH_bO_cN_dS_e(\mathrm{g}) + \left(a + \frac{b}{4} - \frac{c}{2} + e\right)O_2(\mathrm{g})$$

$$= aCO_2(\mathrm{g}) + \frac{b}{2}H_2O(\mathrm{l}) + \frac{d}{2}N_2(\mathrm{g}) + eSO_2(\mathrm{g}) \quad \ldots (E.1)$$

Suppose that the standard enthalpy of combustion at 25 °C, $-H^{\circ}_{S}$ (25 °C), for this reaction is available in authoritative publications (as is indeed the case for all components considered herein). The value of $H^{\circ}_{S}(t)$ at some other temperature t, for this same component j, is then given by the equation

$$[-\overline{H}^{\circ}_{S}(t)]_j = -\overline{H}^{\circ}_{S}(t_0)_j + \sum_k \nu_k \cdot [h^{\circ}_k(t_0) - h^{\circ}_k(t)] \quad \ldots (E.2)$$

or, equivalently,

$$[-\overline{H}^{\circ}_{S}(t)]_j = [-\overline{H}_{S}(t_0)]_j + \sum_k \int_t^{t_0} \nu_k (c^{\circ}_p)_k \, \mathrm{d}t \quad \ldots (E.3)$$

where

t_0 = 25 °C;

$h^{\circ}_k(t)$ is the ideal-gas molar enthalpy;

$(c^{\circ}_p)_k$ is the ideal-gas isobaric molar heat capacity of component k (except for product water which is taken as the liquid). The summation is taken over all components k which appear in the combustion reaction (a maximum of 6 in the most general case);

ν_k is the stoichiometric coefficient for component k, taken as positive for reactants (unity for the "object" component j) and negative for products.

Thus, the calculation is reduced to having sufficient knowledge of either h° or, equivalently, c°_p as a function of temperature, for the "object" component j and the 5 "auxiliary" components O_2, CO_2, N_2 and SO_2 (in the gas phase) and liquid water. Both quantities are complex functions of temperature, most usually expressed in polynomial form, for all components.

Several types of polynomial expression have been used over the years to represent the variation of h° and c°_p with temperature. For the application considered here, the temperature range over which the variation is required is rather small (a maximum of 25 K). Partially as a consequence of this, the entire second term on the right-hand side of equations (E.2) and (E.3) is very small by comparison with the first term, and any reasonable formulation should produce essentially identical results for $\overline{H}^{\circ}_{S}(t)$. Appropriate data for calculating $\overline{H}^{\circ}_{S}(t)$ for specific temperatures may be found for several of the present components (without recourse to polynomial expressions) in the compilations of Armstrong and Jobe[7] and of Garvin *et al.*[8], [10]. Corresponding polynomial expressions given by Passut and Danner[18] or of a modified Wilhoit-Harmens form[19], [20], [21] are also available. Where possible, calculations for $\overline{H}^{\circ}_{S}(t)$ were actually performed by a variety of routes in order to confirm their equivalence. No significant discrepancies were revealed (that is, differences were generally in the second decimal place, which is usually not significant in terms of measurement accuracy and is retained in table 3 only for interpolation).

For the purpose of deriving final values of $\overline{H}^{\circ}_{S}(20\ ^{\circ}\mathrm{C})$, $\overline{H}^{\circ}_{S}(15\ ^{\circ}\mathrm{C})$ and $\overline{H}^{\circ}_{S}(0\ ^{\circ}\mathrm{C})$ from $\overline{H}^{\circ}_{S}(25\ ^{\circ}\mathrm{C})$, to list in table 3, the favoured methods of calculation used data from Garvin *et al.*[8], [10], Armstrong and Jobe[7], or the modified Wilhoit-Harmens polynomial[21], in that order of preference. Further details of these calculations are given in reference [13] in annex M.

E.2 Corrections for non-ideality: volumetric effects

The volume V_m (ideal) occupied, at the metering reference conditions (t_2,p_2), by 1 mol of a gas which behaves in accordance with the so-called ideal gas law (see 2.7) is given by the equation

$$V_\mathrm{m}(\mathrm{ideal}) = \frac{R \cdot T_2}{p_2} \qquad \ldots (\mathrm{E.4})$$

where T_2 is the absolute temperature, in kelvins, equivalent to the Celsius temperature t_2.

No actual gas, and certainly no real natural gas, precisely obeys the ideal gas law: accordingly, the volume V_m(real) occupied by 1 mol of a real gas is often related to V_m(ideal) through use of the quantity Z, known as the compression factor, such that

$$V_\mathrm{m}(\mathrm{real}) = Z(T_2,p_2) \cdot V_\mathrm{m}(\mathrm{ideal}) \qquad \ldots (\mathrm{E.5})$$

$$V_\mathrm{m}(\mathrm{real}) = \frac{Z(T_2,p_2) \cdot R \cdot T_2}{p_2} \qquad \ldots (\mathrm{E.6})$$

The compression factor is generally a function of temperature, pressure and gas composition; it may be greater than or (more often) less than unity, but is usually close to unity for "permanent" gaseous substances.

The theory of statistical mechanics provides both an insight into the general dependence of Z on temperature, pressure and composition, and a means of evaluating it for a mixture of arbitrary composition, from the known properties of the components of the mixture.

The basic statistical mechanical expression for Z is an infinite series of the following form:

$$Z(T,p) = \frac{p \cdot V_\mathrm{m}}{R \cdot T} \qquad \ldots (\mathrm{E.7})$$

$$Z(T,p) = 1 + \frac{B(T)}{V_\mathrm{m}} + \frac{C(T)}{V_\mathrm{m}^2} + \ldots + \frac{Q(T)}{V_\mathrm{m}^{(q-1)}} \qquad \ldots (\mathrm{E.8})$$

where V_m(real) has been abbreviated to V_m for clarity. In this expression, the quantities $B(T)$, $C(T)$, ..., $Q(T)$ are known as the second, third, . . . qth virial coefficients respectively. Each is a function of temperature and composition, but is independent of pressure. The term containing the second virial coefficient accounts for the effect upon Z of two-body molecular interactions (both like-molecule and unlike-molecule); likewise the term containing the third virial coefficient accounts solely for the effects of three-body molecular interactions, and so on. At the pressures of interest in this International Standard, three-body and higher order interactions are unimportant; hence the virial expansion may be truncated at the second term, with no loss of accuracy.

Thus

$$Z_\mathrm{mix} = Z(T,p) = 1 + \frac{B_\mathrm{mix}(T)}{V_\mathrm{m}} \qquad \ldots (\mathrm{E.9})$$

$$Z_\mathrm{mix} = 1 + \frac{p \cdot B_\mathrm{mix}(T)}{Z_\mathrm{mix} \cdot R \cdot T} \qquad \ldots (\mathrm{E.10})$$

Equation (E.10) may be solved as a quadratic in Z_mix if $B_\mathrm{mix}(T)$ is known. The previous text of this subclause is applicable to pure gases and mixtures alike.

Statistical mechanics also provides an expression for B_mix for a multicomponent mixture of arbitrary composition, as follows:

$$B_\mathrm{mix}(T) = \sum_{j}^{N} \sum_{k}^{N} x_j \cdot x_k \cdot B_{jk}(T) \qquad \ldots (\mathrm{E.11})$$

where each summation is taken over all N components of the mixture.

In this expression, there are N like interaction (pure component) terms of the form $x_j^2 \cdot B_{jj}$, and $N(N-1)/2$ unlike (mixed) interaction terms of the form $2x_j \cdot x_k \cdot B_{jk}$ (since the subscripts are theoretically reversible).

It is not practicable to provide numerical values in this International Standard for all B_{jj} (or, equivalently, Z_j) and all B_{jk} for each of the metering temperatures of interest; this would require some 4 620 values, a rather high proportion of which would have to be based on some estimative or correlative technique.

NOTE 21 Calculated as

$$\left[N + \frac{N(N-1)}{2} \right] \times 3$$

for $N = 55$, there being three commonly used values for T_2.

It is clear, then, that a substantial reduction of the data requirement in accordance with a well-understood (and well-behaved) specific approximation is necessary if Z_{mix}, and hence V_{m}(real), are to be readily calculable from equations (E.10) and (E.6). This is especially the case if the method is to be amenable to manual calculation.

One such specific approximation scheme recommended by some authorities[7] is to retain only the N like interaction terms and the $(N - 1)$ unlike interaction terms involving methane as one component (i.e. terms of the form $2x_1 \cdot x_k \cdot B_{1k}$, where the subscript 1 refers to methane). This formulation has the merit of severely reducing the number of terms to be evaluated, and the virial coefficients in those that remain are generally reasonably accessible; moreover, the terms omitted, (i.e. all other $2x_j \cdot x_k \cdot B_{jk}$ terms for $j,k \neq 1$), can reasonably be treated as negligible in many calculations because x_j, $x_k \ll x_1$ for all j, k.

However, for the purpose of this International Standard, an alternative simplification scheme has been preferred which has the advantage of retaining all terms, the like-interaction terms being correctly represented and the unlike-interaction terms being represented in accordance with a specific approximation. The simplification involved may be understood by combining equations (E.9) and (E.11) (omitting T) as follows:

$$Z_{\text{mix}} = 1 + \frac{B_{\text{mix}}}{V_{\text{m}}} \qquad \ldots \text{(E.12)}$$

$$Z_{\text{mix}} = 1 + \sum_j^N \sum_k^N x_j \cdot x_k \times \frac{B_{jk}}{V_{\text{m}}} \qquad \ldots \text{(E.13)}$$

then, making the approximation (for all j,k)

$$\frac{B_{jk}}{V_{\text{m}}} \approx \sqrt{\frac{B_{jj} \cdot B_{kk}}{(V_{\text{m}})_j \cdot (V_{\text{m}})_k}} \qquad \ldots \text{(E.14)}$$

Although having no formal basis in statistical mechanics, this approximation is usually reasonably accurate for mixtures composed of molecules which are not too dissimilar in size, shape and polarity.

Equation (E.13) then becomes

$$Z_{\text{mix}} = 1 + \sum_j^N \sum_k^N x_j \cdot x_k \cdot \sqrt{\frac{B_{jj} \cdot B_{kk}}{(V_{\text{m}})_j \cdot (V_{\text{m}})_k}} \qquad \ldots \text{(E.15)}$$

$$Z_{\text{mix}} = 1 - \sum_j^N \sum_k^N x_j \cdot x_k \cdot \sqrt{(1 - Z_j) \cdot (1 - Z_k)} \qquad \ldots \text{(E.16)}$$

$$Z_{\text{mix}} = 1 - \left[\sum_j^N x_j \cdot \sqrt{b_j} \right]^2 \qquad \ldots \text{(E.17)}$$

where $b_j = 1 - Z_j$.

This expression thus retains all the terms in the original formulation for Z_{mix}, but uses only the values of the pure component compression factors Z_j to do so. Equation (E.17) forms the basis for making corrections for volumetric non-ideality that are both suitable for manual calculations and of sufficient accuracy.

However, equation (E.17) cannot be used in an uncritical way. It is known to have limitations for mixtures containing any of three components, namely hydrogen, helium and carbon dioxide[4]. In the first two cases, this arises because $Z_j > 1$ at metering reference conditions, so that $\sqrt{b}$ is an unreal number (as is also the case for neon). To overcome this, hydrogen, helium and neon are assigned "pseudo"-values of $\sqrt{b}$ and so formally leave equation (E.17) unchanged. For carbon dioxide, there is no need to make such special provisions, provided that its concentration is within the limit of 0,15 mole fraction quoted in clause 1.

NOTE 22 In reference [4] in annex M, which has formed the basis of most subsequent standard documents in this area, an individual treatment is used for any hydrogen present. Specifically, hydrogen is removed from the summation and an extra term added to the overall expression. However, it can be shown that this is not necessary, provided that the hydrogen content of the gas does not exceed 0,05 mole fraction.

Values for all Z_j and $\sqrt{b_j}$ at the three metering reference temperatures of interest are given in table 2 (clause 10). A hierarchy of the means of obtaining these values has been used as follows:

a) Wherever possible, and most obviously for the permanent gases, it is generally preferable to use compression factors taken directly from experiment, or at least from the fitting of high-quality pressure, volume and temperature data to a good interpolative equation of state. The values given in table 2 for such gases have generally been taken from secondary compilations (identified in reference [13] in annex M) which satisfy this criterion.

b) For components which are not gaseous in the pure state at the metering reference conditions, a different approach is required. That generally adopted here is to estimate values for $B(T)$, using the Pitzer-Curl correlation[22], and to convert this value to a "hypothetical" value for $Z(T,p)$ using the pure-gas analogue of equation (E.10). The Pitzer-Curl correlation may be written as

$$\frac{B(T)\cdot p_\mathrm{c}}{R\cdot T_c} = (0{,}144\,5 + 0{,}073\omega) - \frac{0{,}330 - 0{,}46\omega}{T_\mathrm{r}} - \frac{0{,}138\,5 + 0{,}50\omega}{T_\mathrm{r}^2} - \frac{0{,}012\,1 + 0{,}097\omega}{T_\mathrm{r}^3} - \frac{0{,}007\,3\omega}{T_\mathrm{r}^8} \quad \ldots \text{(E.18)}$$

In this expression, the subscript c identifies the value at the gas-liquid critical point, the subscript r identifies the value of a quantity divided by its value at the critical point (i.e. a dimensionless "reduced" value), and ω is the so-called acentric factor. The values used for T_c, p_c and ω are given in clause B.2. In converting values of B to values of Z, the second term on the right-hand side of equation (E.10) has been approximated as $p\cdot B(T)/R\cdot T$.

c) There are a few remaining components which fall outside of the scope of methods a) or b). In particular, the original Pitzer-Curl correlation was developed to apply mostly to hydrocarbons and simple non-polar species. It therefore should not be applied to components such as water, methanol, carbonyl sulfide, etc. A variety of methods, which will not be elaborated here (but which are discussed in reference [13] in annex M), has been used to estimate hypothetical compression factors for such components. Fortunately, none of the components involved will ever be present, in a natural gas or natural gas substitute, in sufficient amounts that any error in Z will propagate detectably into Z_mix.

d) Finally, the special cases of hydrogen, helium and neon have already been mentioned just before note 22. Note that the values listed for Z in table 2 for these components are the true values; only the values for $\sqrt{b}$ are the pseudo-values referred to.

NOTE 23 In current US usage, as exemplified by GPA Standard 2172-86[3], the summation factor $\sqrt{b}$ is effectively defined as $\sqrt{(1-Z)/p}$. The original definition of $\sqrt{b}$ as $\sqrt{1-Z}$ is preferred and retained in this International Standard.

E.3 Corrections for non-ideality: enthalpic effects

The ideal-gas molar superior calorific value $\overline{H}{}_\mathrm{S}^\mathrm{o}$ of $\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_d\mathrm{S}_e$, effectively defined in clause 2 as the negative of the standard enthalpy of combustion of the generalized combustion reaction [equation (E.1)], refers specifically to the ideal reaction; that is, not only is the combustible component assumed to be in the ideal-gas state, but so too are the reactant oxygen and all of the products (except liquid water). A correction to the enthalpy of combustion is therefore in principle required, to account for the fact that combustion reactions cannot actually take place with all components in the ideal-gas state. For a natural gas mixture, the overall combustion process is represented by the mole fraction sum of several equations of the same form as equation (E.1), each having a different set of values for the non-negative integers a,b,c,d,e.

For such a natural gas mixture, for the (initially separate) reactant oxygen and for the homogeneous product mixture, the departure per mole $[h(T,p) - h^\mathrm{o}(T)]$ of the actual enthalpy from the value $h^\mathrm{o}(T)$ in the ideal-gas state at the same temperature, can be calculated if a suitable equation of state is available. For the binary molecular collision (low pressure) approximation it can be shown[7] that in each case, the enthalpy departure is given by the equation

$$\frac{h(T,p,x) - h^\mathrm{o}(T,x)}{R\cdot T} = \frac{B(T,x) - T\left(\dfrac{\mathrm{d}B}{\mathrm{d}T}\right)_x}{V_\mathrm{m}(T,p,x)} \quad \ldots \text{(E.19)}$$

where

$B(T,x)$ is the second virial coefficient for a composition x;

$V_\mathrm{m}(T,p,x)$ is the molar volume, obtainable as the positive solution of the quadratic equation

$$V_\mathrm{m}(T,p,x) = \frac{R\cdot T}{p}\left[1 + \frac{B(T,x)}{V_\mathrm{m}(T,p,x)}\right] \quad \ldots \text{(E.20)}$$

The total enthalpy correction can then be formed as the appropriately weighted sum (i.e. according to stoichiometry) of the three such terms; the contributions from the reactants have to be applied in the opposite sense to that from the products.

Making calculations of this sort is not impossible, but nevertheless is not a practical proposition for manual calculations. Even with computer power available, it is not a trivial task, largely because of the data requirements for the general evaluation of B and its temperature derivative. Fortunately it can be shown[7], by sample calculation, that for natural gas type mixtures under the conditions of interest, the total correction is negligibly small, typically being no greater than 50 J·mol^{-1} (approximately 0,005 %). Enthalpic correction effects are considered no further in this International Standard.

Annex F
(informative)

Effects of water vapour on calorific value

F.1 General

Some calorimeters used for the direct measurement, by combustion, of calorific value per unit volume saturate the fuel gas with water vapour before combustion (during metering), and will therefore measure, and probably (but not necessarily) report, calorific values on an (assumed) saturated basis. Such values are lower than those for the unsaturated (dry or partially saturated) gas, in simple terms, because of the displacement of fuel gas by water vapour in the metering system.

Other instruments used for either the direct or indirect determination of calorific value may not function in an analogous way. For example:

- some direct combustion calorimeters burn the gas on an "as received" basis (i.e. with its prevailing water vapour content) and report the actual calorific value, but on an (assumed) dry basis;
- some instruments dry the gas prior to calorific value determination, and so measure and report a dry gas value even though the gas may originally have contained water vapour;
- instruments for component-analysis of gases (in particular gas-chromatographs) usually analyse for all important components with the single exception of water, and therefore a calculated calorific value is reported on a dry basis, even though the gas may actually contain water vapour.

Therefore, in order to make valid comparisons of gas calorific values determined by different techniques, it is necessary to take into account:

- the degree of saturation with water vapour of the gas in its original state;
- the degree of saturation with water vapour of the gas during the measurement procedure (i.e. after metering);
- the operational characteristics of the measurement instrument or procedure; and
- the degree of saturation with water vapour of the gas referred to in the reported calorific value.

When all of these factors are known, it is possible to refer all determinations of calorific value to a uniform and consistent basis.

Although the main text of this International Standard refers to calculations for the dry gas, it is suggested that the most logical basis in general is the "as received" basis, in which the calorific value is determined, and quoted, with any water vapour present considered as just another component of the mixture, and having a definite mole fraction. There are three considerations to take into account in making calculations if this approach is adopted, especially if analysis for water vapour does not form part of the primary analytical procedure (i.e. if its amount has to be inferred by secondary means, such as hygrometric or dew-point measurements).

F.2 Excluded volume effect

Water may be present in natural gas at a partial pressure p_w of up to its saturation vapour pressure p_s at the reference conditions of the gas metering system. The traditional way of viewing such water vapour is to consider it as excluding a proportion p_w/p_2 of the metering volume from the actual dry fuel gas, thereby reducing the determined calorific value by this proportion to the value

$$\tilde{H}(\text{measured}) = \tilde{H}(\text{dry gas}) \times \frac{p_2 - p_w}{p_2} \qquad \ldots (F.1)$$

where $\tilde{H}$ is the calorific value (either superior or inferior) on a volumetric basis.

An entirely equivalent way of viewing this effect (for purposes of calculation rather than measurement), but preferable because it is more evident that H may now represent the calorific value on either a molar, mass or volumetric basis, is to proceed in terms of mole fractions. Suppose a mole fraction analysis of the gas, excluding any water vapour, is known (as is the assumption for the main text of this International Standard). If the partial pressure of water vapour in the sample is now somehow determined, its mole fraction may be taken as p_w/p_2. In order to retain the sum of the mole fraction of the entire mixture as unity, the mole fraction of each component must be normalized by multiplication by the factor $(p_2 - p_w)/p_2$. Thus, since the calculated calorific value is a summation of linear terms in component mole fractions, the calculated calorific value is simply reduced by this proportion (except for secondary effects referred to in clauses F.3 and F.4), just as is seen from the previous viewpoint.

This primary effect can be important, as the following example shows. Suppose we wish to calculate the calorific value on a saturated-gas basis from a dry-gas analysis, perhaps in order to make a meaningful comparison between the analytically dry-gas calorific value and that determined by a calorimeter which saturates the same gas during metering. Suppose also that the dry-gas volumetric calorific value is 38,00 MJ·m^{-3} at combustion and metering reference conditions of 15 °C, 101,325 kPa. At 15 °C, the saturation vapour pressure is 1,705 kPa, and the mole fraction of water in natural gas saturated with water at the reference conditions is

$$x_w = \frac{1,705}{101,325} = 0,016\ 83 \qquad \ldots \text{(F.2)}$$

Thus, the saturated-gas calorific value (ignoring the secondary effects discussed in clauses F.3 and F.4) is less than the dry-gas calorific value by (1 − 0,016 83), i.e.:

$$\tilde{H}_s = 38,00 \times 0,983\ 17 = 37,36 \text{ MJ·m}^{-3} \qquad \ldots \text{(F.3)}$$

With differences in calorific values of up to 1,68 %, depending on the amount of water vapour present, it is obviously very important to consider the way in which water vapour is accounted for by a measurement or analysis technique. An especially tricky situation can arise for a gas containing water vapour as a known component at below its saturation vapour pressure. In this case, the dry-gas, as received and saturated-gas calorific values are all calculable, all different and all capable of being confused with one another.

F.3 Latent heat (enthalpic) effect

A secondary effect of the presence of water vapour in a sample gas is ignored in clause F.2. The latent heat of vaporization of the water produced by the combustion of hydrocarbons is a significant factor in the determination of the calorific value of those hydrocarbons and, consequently, the state of that water is precisely defined in 2.1 and 2.2.

In the case of the superior calorific value (2.1), it is required that all the water produced by the combustion reaction is condensed to the liquid state at the reference temperature for combustion, t_1. This requirement may be impractical, but it does provide a theoretical basis for the calculation of superior calorific value for a dry natural gas. However, the presence of water vapour in the gas volume prior to combustion presents a problem of how to treat the state of that water after combustion:

a) is it to be assumed, however impractical, that this water remains gaseous after combustion, thus having no effect on the heat of combustion; or

b) is it to be assumed that this water is also condensed to the liquid state at the reference temperature for combustion, t_1, thereby enhancing the heat of combustion by the released latent heat of vaporization of water?

It is suggested that the most logically consistent treatment of the superior calorific value is to assume that all water, both that contained in the gas volume prior to combustion and that produced by combustion, is condensed to the liquid state at the reference temperature for combustion, t_1. Therefore, the water vapour contained in the gas volume is to be treated as a component of the natural gas at a particular mole fraction and having a calorific value derived from the latent heat of vaporization of water; in other words there is another $x_j \cdot H_j$ term in the summation, for water. That is why the superior calorific values for water vapour given in tables 3, 4 and 5 are not zero. Such treatment results in only a small enhancement of calorific value; assuming saturation with water vapour, the enhancement is independent of gas composition and is only dependent on the gas volume (metering) temperature. On a volumetric basis, the enhancement for a saturated gas is

— for metering at 0 °C, an enhancement of 0,01 MJ·m^{-3};

— for metering at 15 °C, an enhancement of 0,03 MJ·m^{-3};

— for metering at 20 °C, an enhancement of 0,045 MJ·m^{-3}.

For inferior calorific value, all water vapour remains in the gas phase, and so there is no enthalpic effect of this type to consider.

F.4 Compression factor effect

There is a third effect that is even more minor, but this should nevertheless be taken into account. The presence of water vapour affects the compression factor of the mixture, and thus alters the real-gas calorific value on a volumetric basis by a calculable amount. At 15 °C, Z is changed from dry to saturated by only about 4 in 10 000 (0,998 1 to 0,997 7) for a typical natural gas.

The main text of this International Standard refers only to the treatment of dry natural gas, as this is recommended as the preferred state. In the event that it is necessary to make calculations for natural gas containing water vapour, however, the points mentioned above should be taken into account when deciding upon a suitable approach.

Annex G
(informative)

Summary, discussion and selection of the calorific value of methane

The enthalpy of combustion of methane is unarguably the single most important physical property value used in the determination of the calorific value of natural gas. Not only is methane the major component of natural gas, but ultra-high purity methane is frequently used as a calibration gas for recording calorimeters routinely used to measure the calorific value of natural gas.

The heat of combustion of methane was first determined in 1848, and since then eight studies have been reported. However, only two sets of values of the standard molar enthalpy of combustion at 25 °C for methane of normal isotopic composition, derived from measurements having claimed levels of accuracy and precision appropriate to present considerations, are available in the scientific literature for conversion to the quantities requiring to be listed in this International Standard.

These two studies are those of Rossini (1931)[23] and of Pittam and Pilcher (1972)[24].

The values of the data points, in chronological order, of these two studies are given below (Rossini's values have been reworked by Armstrong and Jobe[7] in accordance with current molecular mass and temperature scale assignments, etc.).

Rossini kJ·mol^{-1}	**Pittam and Pilcher** kJ·mol^{-1}
– 891,823	– 890,36
– 890,633	– 891,23
– 890,013	– 890,62
– 890,503	– 890,24
– 890,340	– 890,61
– 890,061	– 891,17

In the analysis of his own data, Rossini rejected the highest (first) value as an outlier, which gives a mean of – 890,31 kJ·mol^{-1} ± 0,27 kJ·mol^{-1} based on the remaining five data points. Pittam and Pilcher used all six of their data points to calculate a mean of – 890,71 kJ·mol^{-1} ± 0,41 kJ·mol^{-1}. (The uncertainty figures quoted represent one standard deviation.)

In reviewing the two studies, Armstrong and Jobe concluded that, while they agreed with Rossini's treatment of his own data in rejecting one point as an outlier, if all the data points are taken together as a single set, there is then no clear statistical evidence that any data point(s) should be discarded. Armstrong and Jobe also considered several technical and logistical points which remain valid; these, together with some further points, are as follows.

a) Impurity levels of the methane samples: the sample Rossini used had a measured impurity level of 1 210 ppm carbon monoxide, for which a correction was made, while Pittam and Pilcher used a sample containing less than 5 ppm impurities.

b) Determination of the completeness of reaction: Rossini measured the water formation, the standard method at the time, while Pittam and Pilcher measured the carbon dioxide formation, today's preferred method.

c) Calibration techniques and traceability linkages: Rossini calibrated his calorimeter using an electrical heating method, with traceability to NBS metrology standards, while Pittam and Pilcher used the combustion of hydrogen for calibration purposes, with traceability to Rossini's earlier work on the combustion of hydrogen.

d) Correlation of the heats of formation of the alkane series: an analysis of several heats of formation (derived from heats of combustion) of the lower *n*-alkane homologous series favours the more uniform values, with respect to the CH_2 increment, of Pittam and Pilcher and may suggest a value for methane which is between the values of the two studies.

e) "Sealing" of the calorimeters: Rossini used oil films to "seal" his calorimeter for each individual experiment (re-assembling the calorimeter each time), whereas Pittam and Pilcher claim to have "sealed" their calorimeter for the duration of the test series, but in fact removed a platinum resistance thermometer after each experiment and replaced it with a mercury thermoregulator, with the consequent possibility of water loss.

f) Re-assembly of the calorimeter: Rossini re-assembled his calorimeter prior to each experiment, filling it with a weighed quantity of water, and referred his calibration and combustion to a standard mass of water, whereas Pittam and Pilcher calibrated their calorimeter during a series of experiments and then used that energy equivalent throughout their work, even after the calorimeter had been dismantled, modified and re-assembled, the justification for the continued use of the same energy equivalent apparently being the same mass of water used to refill the calorimeter.

Ultimately, it is difficult, if not impossible, to analyse these various points and to quantify their effects on the data sets in order to decide which of the two should be used or, if both sets of data are to be used, to decide upon weighting factors to use for the individual data points.

Therefore, for the purpose of this International Standard, it has been decided to attribute equal weight importance to each data set, retaining all data points, which results in a standard enthalpy of combustion for methane at 25 °C of − 890,63 kJ·mol^{-1} ± 0,53 kJ·mol^{-1}, with just one data point not within two standard deviations of the mean. This viewpoint is in accordance with the conclusion reached by Garvin in the final report[12] of the project for which the earlier Armstrong and Jobe report[7] was an interim publication.

NOTE 24 Pittam and Pilcher's fourth data point is unfortunately misprinted as − 890,<u>34</u> in reference [7] in annex M; consequently the global mean value given in references [7] and [13] is in error by 0,02 kJ·mol^{-1}.

For convenience, a self-consistent set of resulting calorific values for methane for all of the conditions considered in this International Standard is given in tables G.1 to G.3.

Table G.1 — Calorific value of methane: molar basis

(95 % confidence limit of approximately ± 1,0 kJ·mol^{-1})

Type of calorific value	°C	kJ·mol^{-1}
Superior	25	890,63
Superior	20	891,09
Superior	15	891,56
Superior	0	892,97
Inferior	25	802,60
Inferior	20	802,65
Inferior	15	802,69
Inferior	0	802,82

Table G.2 — Calorific value of methane: mass basis

(95 % confidence limit of approximately ± 0,06 MJ·kg^{-1})

Type of calorific value	°C	MJ·kg^{-1}
Superior	25	55,516
Superior	20	55,545
Superior	15	55,574
Superior	0	55,662
Inferior	25	50,029
Inferior	20	50,032
Inferior	15	50,035
Inferior	0	50,043

Table G.3 — Calorific value of methane: volumetric basis

(95 % confidence limit of approximately ± 0,05 MJ·m^{-3})

Description	MJ·m^{-3}
Ideal Gas, Superior, Combustion at 25 °C, Metering at 0 °C	39,735
Ideal Gas, Superior, Combustion at 15 °C, Metering at 0 °C	39,777
Ideal Gas, Superior, Combustion at 15 °C, Metering at 15 °C	37,706
Ideal Gas, Superior, Combustion at 0 °C, Metering at 0 °C	39,840
Ideal Gas, Superior, Combustion at 20 °C, Metering at 20 °C	37,044
Ideal Gas, Superior, Combustion at 25 °C, Metering at 20 °C	37,024
Ideal Gas, Inferior, Combustion at 25 °C, Metering at 0 °C	35,808
Ideal Gas, Inferior, Combustion at 15 °C, Metering at 0 °C	35,812
Ideal Gas, Inferior, Combustion at 15 °C, Metering at 15 °C	33,948
Ideal Gas, Inferior, Combustion at 0 °C, Metering at 0 °C	35,818
Ideal Gas, Inferior, Combustion at 20 °C, Metering at 20 °C	33,367
Ideal Gas, Inferior, Combustion at 25 °C, Metering at 20 °C	33,365
Real Gas, Superior, Combustion at 25 °C, Metering at 0 °C	39,831
Real Gas, Superior, Combustion at 15 °C, Metering at 0 °C	39,872
Real Gas, Superior, Combustion at 15 °C, Metering at 15 °C	37,782
Real Gas, Superior, Combustion at 0 °C, Metering at 0 °C	39,936
Real Gas, Superior, Combustion at 20 °C, Metering at 20 °C	37,115
Real Gas, Superior, Combustion at 25 °C, Metering at 20 °C	37,095
Real Gas, Inferior, Combustion at 25 °C, Metering at 0 °C	35,894
Real Gas, Inferior, Combustion at 15 °C, Metering at 0 °C	35,898
Real Gas, Inferior, Combustion at 15 °C, Metering at 15 °C	34,016
Real Gas, Inferior, Combustion at 0 °C, Metering at 0 °C	35,904
Real Gas, Inferior, Combustion at 20 °C, Metering at 20 °C	33,431
Real gas, Inferior, Combustion at 25 °C, Metering at 20 °C	33,428

Annex H
(informative)

Derivation of equations relating to precision

Equations (18), (19), (22), (23) and (24) were derived as follows.

H.1 Methane by difference

The fundamental equation given in the main text for the calculation of ideal calorific value (either molar or volumetric) from molar composition is

$$H^{\circ}_{\text{mix}} = \sum_{j=1}^{N} x_j \cdot H^{\circ}_j \qquad \text{. . . (H.1)}$$

In the case where all components except methane are analysed, the methane concentration being calculated by difference, there are actually $N - 1$ independent composition variables x_j, and equation (H.1) may be rewritten as:

$$H^{\circ}_{\text{mix}} = x_1 \cdot H^{\circ}_1 + \sum_{j=2}^{N} x_j \cdot H^{\circ}_j \qquad \text{. . . (H.2)}$$

where

H°_{mix} is the ideal-gas calorific value of the mixture;

x_1 is the mole fraction of methane, given by

$$x_1 = 1 - \sum_{j=2}^{N} x_j$$

where

x_j is the mole fraction of component j;

H°_1 is the ideal-gas calorific value of methane;

H°_j is the ideal-gas calorific value of component j.

Equation (H.2) may be re-arranged, in order to remove the dependent variable x_1, as follows:

$$H^{\circ}_{\text{mix}} = \left(1 - \sum_{j=2}^{N} x_j\right) \cdot H^{\circ}_1 + \sum_{j=2}^{N} x_j \cdot H^{\circ}_j \qquad \text{. . . (H.3)}$$

$$H^{\circ}_{\text{mix}} = H^{\circ}_1 + \sum_{j=2}^{N} x_j \cdot (H^{\circ}_j - H^{\circ}_1) \qquad \text{. . . (H.4)}$$

For each term in the summation we may form the partial derivative as follows:

$$\left(\frac{\partial H^{\circ}_{\text{mix}}}{\partial x_j}\right)_{x_k \neq x_j} = H^{\circ}_j - H^{\circ}_1 \qquad \text{. . . (H.5)}$$

Hence the contribution of the repeatability Δx_j of x_j to the repeatability of H°_{mix} is given by:

$$\Delta (H^{\circ}_{\text{mix}})_j = \Delta x_j \cdot (H^{\circ}_j - H^{\circ}_1) \qquad \text{. . . (H.6)}$$

When all $N - 1$ such terms are combined in quadrature, we obtain equation (18):

$$\Delta H^{\circ}_{\text{mix}} = \left\{ \sum_{j=2}^{N} [\Delta x_j \cdot (H^{\circ}_j - H^{\circ}_1)]^2 \right\}^{1/2} \qquad \text{. . . (H.7)}$$

H.2 Methane by analysis

When all components including methane are analysed, there are N independent composition variables x^*_j, but these do not in general sum to unity as required for input to equation (H.1). In this case, equation (H.1) may be rewritten as

$$H^{\circ}_{\text{mix}} = \frac{\sum_{j=1}^{N} x^*_j \cdot H^{\circ}_j}{\sum_{j=1}^{N} x^*_j} \qquad \text{. . . (H.8)}$$

where

$$x_j = \frac{x_j^*}{\sum_{j=1}^{N} x_j^*} \quad \text{for all } j. \qquad \dots (\text{H.9})$$

For each term in equation (H.8), we may form the partial derivative as follows:

$$\left(\frac{\partial H_{\text{mix}}^{\text{o}}}{\partial x_j^*}\right)_{x_k^* \neq x_j^*} = \frac{H_j^{\text{o}}}{\sum_{j=1}^{N} x_j^*} - \frac{\sum_{j=1}^{N} x_j^* \cdot H_j^{\text{o}}}{\left(\sum_{j=1}^{N} x_j^*\right)^2} \qquad \dots (\text{H.10})$$

or

$$\left(\frac{\partial H_{\text{mix}}^{\text{o}}}{\partial x_j^*}\right)_{x_k^* \neq x_j^*} = \frac{H_j^{\text{o}} - H_{\text{mix}}^{\text{o}}}{K} \qquad \dots (\text{H.11})$$

where

$$K = \sum_{j=1}^{N} x_j^* \qquad \dots (\text{H.12})$$

Hence, ignoring the factor K, which is always close to unity for acceptable experimental results, the contribution of the repeatability Δx_j^* of x_j^* to the repeatability of $H_{\text{mix}}^{\text{o}}$ is given by the equation

$$(\Delta H_{\text{mix}}^{\text{o}})_j = \Delta x_j^* \cdot (H_j^{\text{o}} - H_{\text{mix}}^{\text{o}}) \qquad \dots (\text{H.13})$$

When all N such terms are combined in quadrature, we obtain equation (19):

$$\Delta H_{\text{mix}}^{\text{o}} = \left\{ \sum_{j=1}^{N} [\Delta x_j^* \cdot (H_j^{\text{o}} - H_{\text{mix}}^{\text{o}})]^2 \right\}^{1/2} \qquad \dots (\text{H.14})$$

Note that the component repeatabilities Δx_j^* are those of the non-normalized mole fractions x_j^*, even though $H_{\text{mix}}^{\text{o}}$ itself is calculated using the normalized mole fractions x_j.

This expression may be recast in an alternative form. Equation (H.13) may be rewritten as

$$(\Delta H_{\text{mix}}^{\text{o}})_j = \Delta x_j^* \cdot \left[H_j^{\text{o}}(1 - x_j) - \sum_{k \neq j} x_k \cdot H_k^{\text{o}} \right] \qquad \dots (\text{H.15})$$

When all N such terms are combined in quadrature and re-arranged, we obtain:

$$\Delta H_{\text{mix}}^{\text{o}} = \sqrt{\sum_{j=1}^{N} \left\{ [(1 - x_j) \cdot H_j^{\text{o}} \cdot \Delta x_j^*]^2 - \sum_{k \neq j} [x_j \cdot H_j^{\text{o}} \cdot \Delta x_k^*]^2 \right\}} \qquad \dots (\text{H.16})$$

Note that the component repeatabilities in this expression are again those of the non-normalized mole fractions, although the mole fractions themselves are normalized values.

Equations (22) and (23) were derived using arguments similar to those which led to equations (H.7) and (H.14), respectively.

Equation (24) is obtained by combining in quadrature the relative repeatabilities of the appropriate factors in the defining expression for the ideal Wobbe index, as follows:

$$\frac{\Delta W^{\text{o}}}{W^{\text{o}}} = \left[\left(\frac{\Delta H_{\text{mix}}^{\text{o}}}{H_{\text{mix}}^{\text{o}}} \right)^2 + \left(\frac{\Delta d^{1/2}}{d^{1/2}} \right)^2 \right]^{1/2} \qquad \dots (\text{H.17})$$

which is mathematically identical to the equation

$$\frac{\Delta W^{\text{o}}}{W^{\text{o}}} = \left[\left(\frac{\Delta H_{\text{mix}}^{\text{o}}}{H_{\text{mix}}^{\text{o}}} \right)^2 + \left(\frac{\Delta d}{2d} \right)^2 \right]^{1/2} \qquad \dots (\text{H.18})$$

Annex J

(informative)

Approximate conversion factors between reference states

To obtain the value of a property at the reference condition given in row b) from a known value in the same units at the reference condition given in row a), multiply by the factor indicated in table J.1, J.2. or J.3. To carry out the reverse conversion, divide by the factor indicated. Conversions for properties of the ideal gas are expected to be accurate within ± 0,01 % for all valid compositions. For the real-gas volumetric properties (compression factor, density, relative density) the expected accuracy is ± 0,02 %, and for the real-gas combustion properties (calorific values, Wobbe index) ± 0,1 %.

Table J.1 — Conversion factors for calorific values

	Combustion (°C)		
a) b)	25 to 15	25 to 0	15 to 0
Superior calorific value on a molar basis	1,001 0	1,002 6	1,001 6
Inferior calorific value on a molar basis	1,000 1	1,000 3	1,000 2
Superior calorific value on a mass basis	1,001 0	1,002 6	1,001 6
Inferior calorific value on a mass basis	1,000 1	1,000 3	1,000 2

Table J.2 — Conversion factors for densities, relative densities and compression factor

	Metering (°C)		
a) b)	20 to 15	20 to 0	15 to 0
Ideal density	1,017 4	1,073 2	1,054 9
Ideal relative density	1,000 0	1,000 0	1,000 0
Compression factor	0,999 9	0,999 5	0,999 6
Real density	1,017 5	1,073 8	1,055 3
Real relative density	1,000 1	1,000 3	1,000 2