

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

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Naturgas - Beräkning av värmevärde, densitet, relativ densitet och Wobbe-index baserat på gassammansättningen

Denna standard utgörs av den engelska versionen av den internationella standarden ISO 6976:1995.

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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 0,00005 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 $\bar{H}_S(t_1, p_1)$; 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 $H_S[t_1, p_1, V(t_2, p_2)]$, 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 $\bar{H}_I(t_1, p_1)$, $\hat{H}_I(t_1, p_1)$ and $H_I[t_1, p_1, V(t_2, p_2)]$.

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.

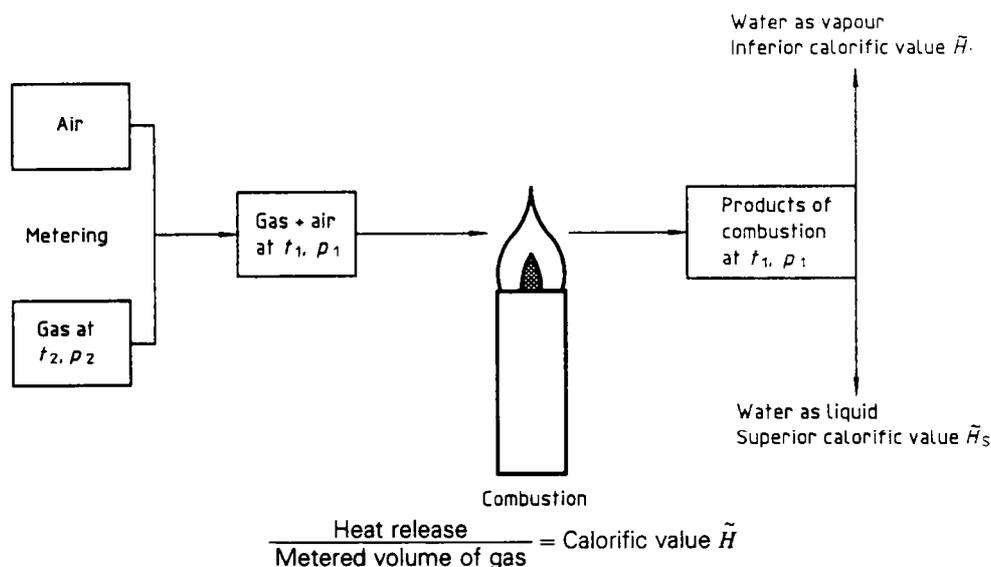


Figure 1 — Calorific value on a volumetric basis — Metering and combustion reference conditions

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

$$p \cdot V_m = R \cdot T \quad \dots (1)$$

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

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

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 corre-

sponding 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 $t_1 = 25 \text{ }^\circ\text{C}$, $20 \text{ }^\circ\text{C}$, $15 \text{ }^\circ\text{C}$ and $0 \text{ }^\circ\text{C}$. 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 em-

ployed 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):

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

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

$$\bar{H}^{\circ}(t_1) = \sum_{j=1}^N x_j \bar{H}_j^{\circ}(t_1) \quad \dots (4)$$

where

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

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

Values for \bar{H}_j° for other temperatures ($t_1 = 20 \text{ }^{\circ}\text{C}$, $15 \text{ }^{\circ}\text{C}$ and $0 \text{ }^{\circ}\text{C}$) are also given in table 3; these values

have been derived from the $25 \text{ }^{\circ}\text{C}$ values in accordance with the methods described in clause E. 1.

NOTES

11 Values of \bar{H}_j° are independent of pressure; consequently the combustion reference pressure p_i 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 $50 \text{ J}\cdot\text{mol}^{-1}$ (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

$$\hat{H}^{\circ}(t_1) = \frac{\bar{H}^{\circ}(t_1)}{M} \quad \dots (5)$$

where

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

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

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}° . An alternative method uses the equation

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

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° 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 \bar{H}_j° 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

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

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}° . An alternative method uses the equation

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

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° 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 \bar{H}_j° 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

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

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

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

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

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

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

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

where

- W° is the Wobbe index of the ideal gas;
- \tilde{H}_S° is calculated as described in 7.1.

8.2 Real gas

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

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

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

$$Z_{\text{air}}(273,15 \text{ K}, 101,325 \text{ kPa}) = 0,99941$$

$$Z_{\text{air}}(288,15 \text{ K}, 101,325 \text{ kPa}) = 0,99958$$

$$Z_{\text{air}}(293,15 \text{ K}, 101,325 \text{ kPa}) = 0,99963$$

The density of the real gas is calculated from the equation

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

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

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

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

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

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

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

Y_i is the value of the physical property calculated from the i th 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

$$\Delta H_{\text{mix}}^{\circ} = \left\{ \sum_{j=2}^N [\Delta x_j \cdot (H_j^{\circ} - H_1^{\circ})]^2 \right\}^{1/2} \dots (18)$$

where

$\Delta H_{\text{mix}}^{\circ}$ 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_1^0 is the ideal-gas calorific value of methane.

b) When all components including methane are analysed, then

$$\Delta H_{\text{mix}}^0 = \left\{ \sum_{j=1}^N [\Delta x_j \cdot (H_j^0 - H_{\text{mix}}^0)]^2 \right\}^{1/2} \quad \dots (19)$$

where, although H_{mix}^0 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:

$$\Delta d = \frac{\Delta M}{M_{\text{air}}} \quad \dots (20)$$

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

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

— for case a):

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

— For case b):

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

where M_j is the molar mass of component j .

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

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

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 A - f , d , p 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 , p 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 systematic error, viz.

- uncertainties in the basic data given in tables 1 to 5;
- bias in the method of calculation which uses these data;
- 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:		0,0001
Density:		0,0001 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.