



BSI Standards Publication

Natural gas - Calculation of thermodynamic properties

Part 1: Gas phase properties for transmission and distribution applications

National foreword

This British Standard is the UK implementation of EN ISO 20765-1:2018. It is identical to ISO 20765-1:2005. It supersedes BS ISO 20765-1:2005, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee GSE/26, Test gases.

A list of organizations represented on this committee can be obtained on request to its secretary.

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31 October 2018	This corrigendum renumbers BS ISO 20765-1:2005 as BS EN ISO 20765-1:2018

English Version

Natural gas - Calculation of thermodynamic properties -
Part 1: Gas phase properties for transmission and
distribution applications (ISO 20765-1:2005)

Gaz naturel - Calcul des propriétés thermodynamiques
- Partie 1: Propriétés de la phase gazeuse pour des
applications de transport et de distribution (ISO
20765-1:2005)

Erdgas - Berechnung thermodynamischer
Eigenschaften - Teil 1: Eigenschaften der Gasphase für
Zwecke des Transports und der Verteilung (ISO 20765-
1:2005)

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European foreword

The text of ISO 20765-1:2005 has been prepared by Technical Committee ISO/TC 193 "Natural gas" of the International Organization for Standardization (ISO) and has been taken over as EN ISO 20765-1:2018 by Technical Committee CEN/TC 238 "Test gases, test pressures, appliance categories and gas appliance types" the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2019, and conflicting national standards shall be withdrawn at the latest by March 2019.

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Endorsement notice

The text of ISO 20765-1:2005 has been approved by CEN as EN ISO 20765-1:2018 without any modification.

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Foreword

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

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

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 20765-1 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

ISO 20765 consists of the following parts, under the general title *Natural gas — Calculation of thermodynamic properties*:

— *Part 1: Gas phase properties for transmission and distribution applications*

The following parts are under preparation:

— *Part 2: Single phase properties (gas, liquid and dense-fluid) for extended ranges of application*

— *Part 3: Two-phase properties (vapour-liquid equilibria)*

Introduction

This part of ISO 20765 specifies methods for the calculation of thermodynamic properties of natural gases, natural gases containing synthetic admixture, and similar mixtures.

This part of ISO 20765 has four normative annexes and three informative annexes.

Natural gas — Calculation of thermodynamic properties —

Part 1: Gas phase properties for transmission and distribution applications

1 Scope

This part of ISO 20765 specifies a method of calculation for the volumetric and caloric properties of natural gases, natural gases containing synthetic admixture and similar mixtures, at conditions where the mixture can exist only as a gas.

The method is applicable to pipeline-quality gases within the ranges of pressure, p , and temperature, T , at which transmission and distribution operations normally take place. For volumetric properties (compression factor and density), the uncertainty of calculation is about $\pm 0,1\%$ (95 % confidence interval). For caloric properties (for example enthalpy, heat capacity, Joule-Thomson coefficient, speed of sound), the uncertainty of calculation is usually greater.

2 Normative references

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

ISO 31-3, *Quantities and units — Part 3: Mechanics*

ISO 31-4, *Quantities and units — Part 4: Heat*

ISO 7504, *Gas analysis — Vocabulary*

ISO 12213-2, *Natural gas — Calculation of compression factor — Part 2: Calculation using molar-composition analysis*

ISO 14532, *Natural gas — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 31-4, ISO 7504 and ISO 14532 and the following apply.

NOTE See Annex A for the list of symbols and units used in this part of ISO 20765.

3.1

caloric property

characteristic of a gas or homogeneous gas mixture which can be calculated from a fundamental equation of state

NOTE The caloric properties to which this part of ISO 20765 can be applied are internal energy, enthalpy, entropy, isochoric heat capacity, isobaric heat capacity, Joule-Thomson coefficient, isentropic exponent and speed of sound.

3.2

equation of state

mathematical relationship between state variables of a gas or homogeneous gas mixture

NOTE In this part of ISO 20765, it is useful to distinguish between two types of equation of state, namely (1) volumetric equation of state, in which the relationship is between the state variables pressure, temperature and the volume occupied by a given amount of substance, and (2) fundamental equation of state, in which the relationship is between the density, temperature and the Helmholtz free energy.

3.3

residual property

that part of a thermodynamic property which results from the non-ideal (real-gas) behaviour of a gas or homogeneous gas mixture, i.e. the difference between a thermodynamic property of a real gas or gas mixture and the same thermodynamic property for the same gas or gas mixture, in the ideal state, at the same state conditions of temperature and density

3.4

thermodynamic property

volumetric or caloric property

3.5

volumetric property

characteristic of a gas or homogeneous gas mixture that can be calculated from a volumetric equation of state

NOTE The volumetric properties to which this part of ISO 20765 can be applied are compression factor and density.

4 Thermodynamic basis of the method

4.1 Principle

The method recommended is based on the concept that pipeline-quality natural gas is completely characterized for the calculation of its thermodynamic properties by component analysis. Such an analysis, together with the state variables of temperature and density, provides the necessary input data for the method. In practice, the state variables available as input data are more usually temperature and pressure and, in this case, it is necessary first to convert these to temperature and density.

Equations are presented which express the Helmholtz free energy of the gas as a function of density, temperature and composition, from which all of the thermodynamic properties can be obtained in terms of the Helmholtz free energy and its derivatives with respect to temperature and density.

The method uses a detailed molar composition analysis in which all components present in amounts exceeding 0,000 05 mole fraction [50 molar ppm¹⁾] should be represented. For a typical natural gas, this might include alkane hydrocarbons up to about C₇ or C₈, together with nitrogen, carbon dioxide and helium. Typically, isomers for alkanes above C₅ may be lumped together by molecular weight and treated collectively as the normal isomer.

For some natural gases, it may be necessary to take into consideration additional components such as C₉ and C₁₀ hydrocarbons, water vapour and hydrogen sulfide. For manufactured gases, hydrogen and carbon monoxide should be considered.

More precisely, the method uses a 21-component analysis in which all of the major and minor components of natural gas are included (see 6.2). Any trace component present but not identified as one of the 21 specified components may be reassigned appropriately to a specified component.

¹⁾ ppm is a deprecated unit.

4.2 The fundamental equation of Helmholtz free energy

4.2.1 Background

The AGA8 equation [1] was published in 1992 by the Transmission Measurements Committee of the American Gas Association, having been designed specifically as a means for the high accuracy calculation of compression factor. In this respect, it is already the subject of ISO 12213-2. Since then it has become increasingly apparent that the equation has excellent potential for use in the calculation of all thermodynamic properties of natural gas, even though the accuracy of calculation is less well documented.

In order for the AGA8 equation to become useful for the calculation of all thermodynamic properties, there are two major requirements.

- The equation itself, published initially in a form explicit only for volumetric properties, has to be mathematically recast in a form explicit for the residual Helmholtz free energy. In fact, although not published as such, the original development of the equation was as a fundamental equation in the form of Helmholtz free energy. This formulation [2] is essential in that all residual thermodynamic properties can be calculated from the Helmholtz free energy and its derivatives with respect to the state conditions of temperature and density.
- For the calculation of caloric properties, a formulation is required for the Helmholtz free energy of the ideal gas as a function of temperature. Most previous formulations for the ideal gas have been explicit in the isobaric heat capacity and so, again, the chosen formulation [3], [4] has to be recast so as to be explicit in the Helmholtz free energy. Again, derivatives of the Helmholtz free energy with respect to the state conditions are needed.

An important aspect of the formulations chosen for both the ideal and residual parts of the Helmholtz free energy is that the derivatives required for calculating the thermodynamic properties can be given in analytical form. Hence, there is no need for numerical differentiation or integration within any computer program that implements the procedures. As a result, numerical problems are avoided and calculation times are shorter.

The method of calculation described is very suitable for use within process simulation programs and, in particular, within programs developed for use in natural gas transmission and distribution applications.

4.2.2 The Helmholtz free energy

The Helmholtz free energy, f , of a homogeneous gas mixture at uniform pressure and temperature can be expressed as the sum of a part f_o describing the ideal gas behaviour and a part f_r describing the residual or real-gas behaviour, as given in Equation (1):

$$f(\rho, T, X) = f_o(\rho, T, X) + f_r(\rho, T, X) \quad (1)$$

which, rewritten in the form of dimensionless reduced free energy $\phi = f/(R \cdot T)$, becomes Equation (2):

$$\phi(\delta, \tau, X) = \phi_o(\delta, \tau, X) + \phi_r(\delta, \tau, X) \quad (2)$$

where

X is a vector that defines the composition of the mixture;

τ is the inverse (dimensionless) reduced temperature, related to the temperature, T , as given in Equation (3):

$$\tau = L/T \quad (3)$$

where $L = 1 \text{ K}$.

Note that Equations (1) and (2) are written in terms of the molar density, ρ , and reduced density, δ , respectively, not in terms of the more commonly available input variable of pressure, p . This is because, from statistical thermodynamics, the Helmholtz free energy appears as a natural consequence of the number and types of molecular interactions in a mixture and, therefore, becomes a natural function of the molar density and mole fractions of the molecules.

The reduced density, δ , is related to the molar density, ρ , as shown in Equation (4):

$$\delta = K^3 \cdot \rho \quad (4)$$

where K is a mixture size parameter.

The ideal part, ϕ_o , of the reduced Helmholtz free energy is obtained from equations for the isobaric heat capacity in the ideal gas state (see 4.2.3), and the residual part, ϕ_{ris} , from the AGA8 equation of state (see 4.2.4).

4.2.3 The Helmholtz free energy of the ideal gas

The Helmholtz free energy of an ideal gas can be expressed in terms of the enthalpy, h_o , and entropy, s_o , as given in Equation (5):

$$f_o(\rho, T, X) = h_o(T, X) - R \cdot T - T \cdot s_o(\rho, T, X) \quad (5)$$

The enthalpy, h_o , and entropy, s_o , can in turn be expressed in terms of the isobaric heat capacity, $c_{o,p}$, of the ideal gas as given in Equations (6) and (7), where the implied limits of integration are T_θ and T :

$$h_o(T, X) = \int c_{o,p} dT + h_{o,\theta} \quad (6)$$

$$s_o(\rho, T, X) = \int \frac{c_{o,p}}{T} dT - R \cdot \ln\left(\frac{\rho}{\rho_\theta}\right) - R \cdot \ln\left(\frac{T}{T_\theta}\right) + s_{o,\theta} - R \cdot \sum_{i=1}^N x_i \cdot \ln x_i \quad (7)$$

The reference state of zero enthalpy and zero entropy is here adopted as $T_\theta = 298,15 \text{ K}$ and $p_\theta = 0,101\,325 \text{ MPa}$ for the ideal unmixed gas. The integration constants, $h_{o,\theta}$ and $s_{o,\theta}$, are then determined so as to conform to this definition. The reference (ideal) density, ρ_θ , is given by $\rho_\theta = p_\theta / (R \cdot T_\theta)$.

The reduced Helmholtz free energy $\phi_o = f_o / (R \cdot T)$ can then be written, using Equations (6) and (7), as a function of δ , τ and X , as given in Equation (8):

$$\phi_o(\delta, \tau, X) = -\tau \int \frac{c_{o,p}}{R \cdot \tau^2} d\tau + \frac{h_{o,\theta} \cdot \tau}{R \cdot L} - 1 + \int \frac{c_{o,p}}{R \cdot \tau} d\tau + \ln\left(\frac{\delta}{\delta_\theta}\right) + \ln\left(\frac{\tau_\theta}{\tau}\right) - \frac{s_{o,\theta}}{R} + \sum_{i=1}^N x_i \cdot \ln x_i \quad (8)$$

See Annex B for details of this formulation.

4.2.4 The residual part of the Helmholtz free energy

The residual part of the reduced Helmholtz free energy is obtained, for the purposes of this part of ISO 20765, by use of the AGA8 equation. Written for the compression factor as a function of reduced density, inverse reduced temperature and composition, the AGA8 equation has the form of Equation (9):

$$Z = 1 + \frac{B \cdot \delta}{K^3} - \delta \sum_{n=13}^{18} C_n \cdot \tau^{u_n} + \sum_{n=13}^{58} C_n \cdot \tau^{u_n} \cdot \delta^{b_n} \left(b_n - c_n \cdot k_n \cdot \delta^{k_n} \right) \exp\left(-c_n \cdot \delta^{k_n}\right) \quad (9)$$

where

B is the second virial coefficient;

b_n, c_n, k_n, u_n are coefficients of the equation and functions of composition;

C_n is a function of composition.

The compression factor, Z , is related to the residual part of reduced free energy, φ_r , as given in Equation (10):

$$Z = 1 + \delta \cdot \varphi_{r,\delta} \quad (10)$$

where $\varphi_{r,\delta}$ is the partial derivative of φ_r with respect to reduced density at constant τ and X .

Elimination of Z between Equations (9) and (10), and integration with respect to reduced density leads to the Equation (11) for the residual part of the reduced Helmholtz free energy:

$$\varphi_r(\delta, \tau, X) = \frac{B \cdot \delta}{K^3} - \delta \sum_{n=13}^{18} C_n \cdot \tau^{u_n} + \sum_{n=13}^{58} C_n \cdot \tau^{u_n} \cdot \delta^{b_n} \exp(-c_n \cdot \delta^{k_n}) \quad (11)$$

See Annexes C and D for details of this formulation.

4.2.5 The reduced Helmholtz free energy

The fundamental equation [Equation (2)] for the reduced Helmholtz free energy, φ , makes it possible, through use of Equation (8) for the ideal part, φ_o , and Equation (11) for the residual part, φ_r , to calculate all thermodynamic properties analytically. The reduced Helmholtz free energy, φ , therefore can be written as given in Equation (12):

$$\begin{aligned} \varphi(\delta, \tau, X) = & -\tau \int \frac{c_{o,p}}{R \cdot \tau^2} d\tau + \frac{h_{o,\theta} \cdot \tau}{R} - 1 + \int \frac{c_{o,p}}{R \cdot \tau} d\tau + \ln\left(\frac{\delta}{\delta_\theta}\right) + \ln\left(\frac{\tau_\theta}{\tau}\right) - \frac{s_{o,\theta}}{R} + \sum_{i=1}^N x_i \cdot \ln x_i + \dots \\ & \dots + \frac{B \cdot \delta}{K^3} - \delta \sum_{n=13}^{18} C_n \cdot \tau^{u_n} + \sum_{n=13}^{58} C_n \cdot \tau^{u_n} \cdot \delta^{b_n} \exp(-c_n \cdot \delta^{k_n}) \end{aligned} \quad (12)$$

4.3 Thermodynamic properties derived from the Helmholtz free energy

4.3.1 Background

All of the thermodynamic properties can be written explicitly in terms of the reduced Helmholtz free energy, φ , and various derivatives thereof. The required derivatives, φ_τ , $\varphi_{\tau\tau}$, φ_δ , $\varphi_{\delta\delta}$ and $\varphi_{\tau\delta}$, are defined as given in Equations (13):

$$\varphi_\tau = \left(\frac{\partial \varphi}{\partial \tau} \right)_{\delta, X} \quad \varphi_{\tau\tau} = \left(\frac{\partial^2 \varphi}{\partial \tau^2} \right)_{\delta, X} \quad \varphi_\delta = \left(\frac{\partial \varphi}{\partial \delta} \right)_{\tau, X} \quad \varphi_{\delta\delta} = \left(\frac{\partial^2 \varphi}{\partial \delta^2} \right)_{\tau, X} \quad \varphi_{\tau\delta} = \left[\frac{\partial}{\partial \tau} \left(\frac{\partial \varphi}{\partial \delta} \right) \right]_{\tau, X} \bigg|_{\delta, X} \quad (13)$$

Each derivative is the sum of an ideal part (see Annex B) and a residual part (see Annex C). The substitutions given in Equations (14) and (15) help to simplify the appearance of the relevant relationships:

$$\varphi_1 = \left[\frac{\partial(\delta^2 \cdot \varphi_\delta)}{\partial \delta} \right]_{\tau, X} = 2 \cdot \delta \cdot \varphi_\delta + \delta^2 \cdot \varphi_{\delta\delta} \quad (14)$$

$$\varphi_2 = -\tau^2 \left[\frac{\partial}{\partial \tau} \left(\frac{\delta \cdot \varphi_\delta}{\tau} \right) \right]_{\delta, X} = \delta \cdot \varphi_\delta - \tau \cdot \delta \cdot \varphi_{\tau\delta} \quad (15)$$

Detailed expressions for φ_τ , $\varphi_{\tau\tau}$, φ_δ , φ_1 and φ_2 can be found in Annex C.

The relevant general relationships for the various thermodynamic properties are given in 4.3.2.1 to 4.3.2.9 [Equations (17) to (26)]. In Equations (19) to (24), lowercase symbols represent molar quantities (i.e. quantity per mole) and the corresponding upper case symbols represent specific quantities (i.e. quantity per kilogram). Conversion of molar variables to mass-basis variables is achieved by division by the molar mass M .

NOTE In these equations, R is the molar gas constant; consequently R/M is the specific gas constant.

The molar mass, M , of the mixture is derived from the composition, X , and molar masses, M_i , of the pure substances as given in Equation (16):

$$M = \sum_{i=1}^N x_i \cdot M_i \quad (16)$$

Values for molar masses, M_i , of pure substances are given in References [1] and [2]; these values are identical with those given in ISO 6976:1995 [5].

NOTE The values given in ISO 6976 for the molar masses are in most cases not identical with the most recent values adopted by the international community of metrologists. They are, however, the values that were in general use during the development of the AGA8 equation, and are therefore retained here; the differences are in all cases less than 0,001 kg/kmol.

In Equations (20), (21) and (23) to (26), the basic expressions for the properties h , s , c_p , μ , κ and w have been transformed in several ways, such that values of properties already derived can be used to simplify the subsequent calculations. This approach is useful for applications where several or all of the thermodynamic properties are to be determined. For clarity, the basic thermodynamic relationships are given first in each subclause, and the subsidiary transformations are given below.

4.3.2 Equations for thermodynamic properties

4.3.2.1 Compression factor and density

The expression for the compression factor, Z , is given by Equation (17):

$$Z = \delta \cdot \varphi_\delta \quad (17)$$

where φ_δ is the derivative with respect to the reduced molar density of the Helmholtz free energy [see also Equation (10)]. The molar density, ρ , and specific (mass) density, D , are related to pressure as given in Equation (18):

$$\rho = D/M = p/(Z \cdot R \cdot T) \quad (18)$$

Values of compression factor, Z , calculated in accordance with this part of ISO 20765 should normally be identical with values calculated in accordance with ISO 12213-2. In any case where a requirement for priority is identified, ISO 12213-2 shall take precedence.

4.3.2.2 Internal energy

The expression for the internal energy, u , is given by Equation (19):

$$\frac{u}{R \cdot T} = \frac{U \cdot M}{R \cdot T} = \tau \cdot \varphi_\tau \quad (19)$$

4.3.2.3 Enthalpy

The expression for the enthalpy, h , is given by Equation (20):

$$\begin{aligned}\frac{h}{R \cdot T} &= \frac{H \cdot M}{R \cdot T} \\ &= \tau \cdot \varphi_{\tau} + \delta \cdot \varphi_{\delta} \\ &= \frac{u}{R \cdot T} + Z = \frac{U \cdot M}{R \cdot T} + Z\end{aligned}\quad (20)$$

4.3.2.4 Entropy

The expression for the entropy, s , is given by Equation (21):

$$\begin{aligned}\frac{s}{R} &= \frac{S \cdot M}{R} \\ &= \tau \cdot \varphi_{\tau} - \varphi \\ &= \frac{u}{R \cdot T} - \varphi = \frac{U \cdot M}{R \cdot T} - \varphi\end{aligned}\quad (21)$$

4.3.2.5 Isochoric heat capacity

The expression for the isochoric heat capacity, c_v , is given by Equation (22):

$$\frac{c_v}{R} = \frac{C_v \cdot M}{R} = -\tau^2 \cdot \varphi_{\tau\tau} \quad (22)$$

4.3.2.6 Isobaric heat capacity

The expression for the isobaric heat capacity, c_p , is given by Equation (23):

$$\begin{aligned}\frac{c_p}{R} &= \frac{C_p \cdot M}{R} \\ &= -\tau^2 \cdot \varphi_{\tau\tau} + \frac{\varphi_2^2}{\varphi_1} \\ &= \frac{c_v}{R} + \frac{\varphi_2^2}{\varphi_1} \\ &= \frac{C_v \cdot M}{R} + \frac{\varphi_2^2}{\varphi_1}\end{aligned}\quad (23)$$

4.3.2.7 Joule-Thomson coefficient

The expression for the Joule-Thomson coefficient, μ , is given by Equation (24):

$$\begin{aligned}\mu \cdot R \cdot \rho &= \frac{\mu \cdot R \cdot D}{M} \\ &= \frac{\varphi_2 - \varphi_1}{\varphi_2^2 - \left(\tau^2 \cdot \varphi_{\tau\tau} \cdot \varphi_1 \right)} \\ &= \frac{R}{c_p} \left(\frac{\varphi_2}{\varphi_1} - 1 \right) \\ &= \frac{R}{C_p \cdot M} \left(\frac{\varphi_2}{\varphi_1} - 1 \right)\end{aligned}\quad (24)$$