
**Natural gas — Calculation of
thermodynamic properties —**

Part 2:

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

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Gaz naturel — Calcul des propriétés thermodynamiques —

*Partie 2: Propriétés des phases uniques (gaz, liquide, fluide dense)
pour une gamme étendue d'applications*

<https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015>



iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 20765-2:2015

<https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2015

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

	Page
Foreword	v
1 Scope	1
2 Normative references	2
3 Terms and definitions	2
4 Thermodynamic basis of the method	4
4.1 Principle	4
4.2 The fundamental equation based on the Helmholtz free energy	4
4.2.1 Background	4
4.2.2 The Helmholtz free energy	5
4.2.3 The reduced Helmholtz free energy	5
4.2.4 The reduced Helmholtz free energy of the ideal gas	6
4.2.5 The pure substance contribution to the residual part of the reduced Helmholtz free energy	6
4.2.6 The departure function contribution to the residual part of the reduced Helmholtz free energy	7
4.2.7 Reducing functions	8
4.3 Thermodynamic properties derived from the Helmholtz free energy	8
4.3.1 Background	8
4.3.2 Relations for the calculation of thermodynamic properties in the homogeneous region	9
5 Method of calculation	11
5.1 Input variables	11
5.2 Conversion from pressure to reduced density	11
5.3 Implementation	12
6 Ranges of application	13
6.1 Pure gases	13
6.2 Binary mixtures	14
6.3 Natural gases	17
7 Uncertainty of the equation of state	18
7.1 Background	18
7.2 Uncertainty for pure gases	18
7.2.1 Natural gas main components	18
7.2.2 Secondary alkanes	19
7.2.3 Other secondary components	21
7.3 Uncertainty for binary mixtures	21
7.4 Uncertainty for natural gases	23
7.4.1 Uncertainty in the normal and intermediate ranges of applicability of natural gas	24
7.4.2 Uncertainty in the full range of applicability, and calculation of properties beyond this range	25
7.5 Uncertainties in other properties	25
7.6 Impact of uncertainties of input variables	25
8 Reporting of results	25
Annex A (normative) Symbols and units	27
Annex B (normative) The reduced Helmholtz free energy of the ideal gas	29
Annex C (normative) Values of critical parameters and molar masses of the pure components	35
Annex D (normative) The residual part of the reduced Helmholtz free energy	36
Annex E (normative) The reducing functions for density and temperature	48
Annex F (informative) Assignment of trace components	55

Annex G (informative) Examples	57
Bibliography	60

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 20765-2:2015](https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015)

<https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015>

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#)

The committee responsible for this document is 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*
- *Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application*
- *Part 3: Two-phase properties (vapour-liquid equilibria)*

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 20765-2:2015

<https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015>

Natural gas — Calculation of thermodynamic properties —

Part 2:

Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application

1 Scope

This part of ISO 20765 specifies a method to calculate volumetric and caloric properties of natural gases, manufactured fuel gases, and similar mixtures, at conditions where the mixture may be in either the homogeneous (single-phase) gas state, the homogeneous liquid state, or the homogeneous supercritical (dense-fluid) state.

NOTE 1 Although the primary application of this document is to natural gases, manufactured fuel gases, and similar mixtures, the method presented is also applicable with high accuracy (i.e., to within experimental uncertainty) to each of the (pure) natural gas components and to numerous binary and multi-component mixtures related to or not related to natural gas.

For mixtures in the gas phase and for both volumetric properties (compression factor and density) and caloric properties (for example, enthalpy, heat capacity, Joule-Thomson coefficient, and speed of sound), the method is at least equal in accuracy to the method described in Part 1 of this International Standard, over the full ranges of pressure p , temperature T , and composition to which Part 1 applies. In some regions, the performance is significantly better; for example, in the temperature range 250 K to 275 K (−10 °F to 35 °F). The method described here maintains an uncertainty of $\leq 0,1$ % for volumetric properties, and generally within 0,1 % for speed of sound. It accurately describes volumetric and caloric properties of homogeneous gas, liquid, and supercritical fluids as well as those in vapour-liquid equilibrium. Therefore its structure is more complex than that in Part 1.

NOTE 2 All uncertainties in this document are expanded uncertainties given for a 95 % confidence level (coverage factor $k = 2$).

The method described here is also applicable with no increase in uncertainty to wider ranges of temperature, pressure, and composition for which the method of Part 1 is not applicable. For example, it is applicable to natural gases with lower content of methane (down to 0,30 mole fraction), higher content of nitrogen (up to 0,55 mole fraction), carbon dioxide (up to 0,30 mole fraction), ethane (up to 0,25 mole fraction), and propane (up to 0,14 mole fraction), and to hydrogen-rich natural gases. A practical usage is the calculation of properties of highly concentrated CO₂ mixtures found in carbon dioxide sequestration applications.

The mixture model presented here is valid by design over the entire fluid region. In the liquid and dense-fluid regions the paucity of high quality test data does not in general allow definitive statements of uncertainty for all sorts of multi-component natural gas mixtures. For saturated liquid densities of LNG-type fluids in the temperature range from 100 K to 140 K (−280 °F to −208 °F), the uncertainty is $\leq (0,1 - 0,3)$ %, which is in agreement with the estimated experimental uncertainty of available test data. The model represents experimental data for compressed liquid densities of various binary mixtures to within $\pm(0,1 - 0,2)$ % at pressures up to 40 MPa (5800 psia), which is also in agreement with the estimated experimental uncertainty. Due to the high accuracy of the equations developed for the binary subsystems, the mixture model can predict the thermodynamic properties for the liquid and dense-fluid regions with the best accuracy presently possible for multi-component natural gas fluids.

2 Normative references

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

ISO 7504, *Gas Analysis — Vocabulary*

ISO 14532, *Natural gas — Vocabulary*

ISO 20765-1, *Natural gas — Calculation of thermodynamic properties — Part 1: Gas phase properties for transmission and distribution applications*

ISO 80000-5:2007, *Quantities and units — Part 5: Thermodynamics*

3 Terms and definitions

For the purposes of this document, the terms and definitions in ISO 80000-5:2007 and/or ISO 20765-1, ISO 7504, ISO 14532, and the following apply.

NOTE 1 See [Annex A](#) for the list of symbols and units used in this part of ISO 20765.

NOTE 2 [Figure 1](#) is a schematic representation of the phase behaviour of a typical natural gas as a function of pressure and temperature. The positions of the bubble and dew lines depend upon the composition. This phase diagram may be useful in understanding the definitions below.

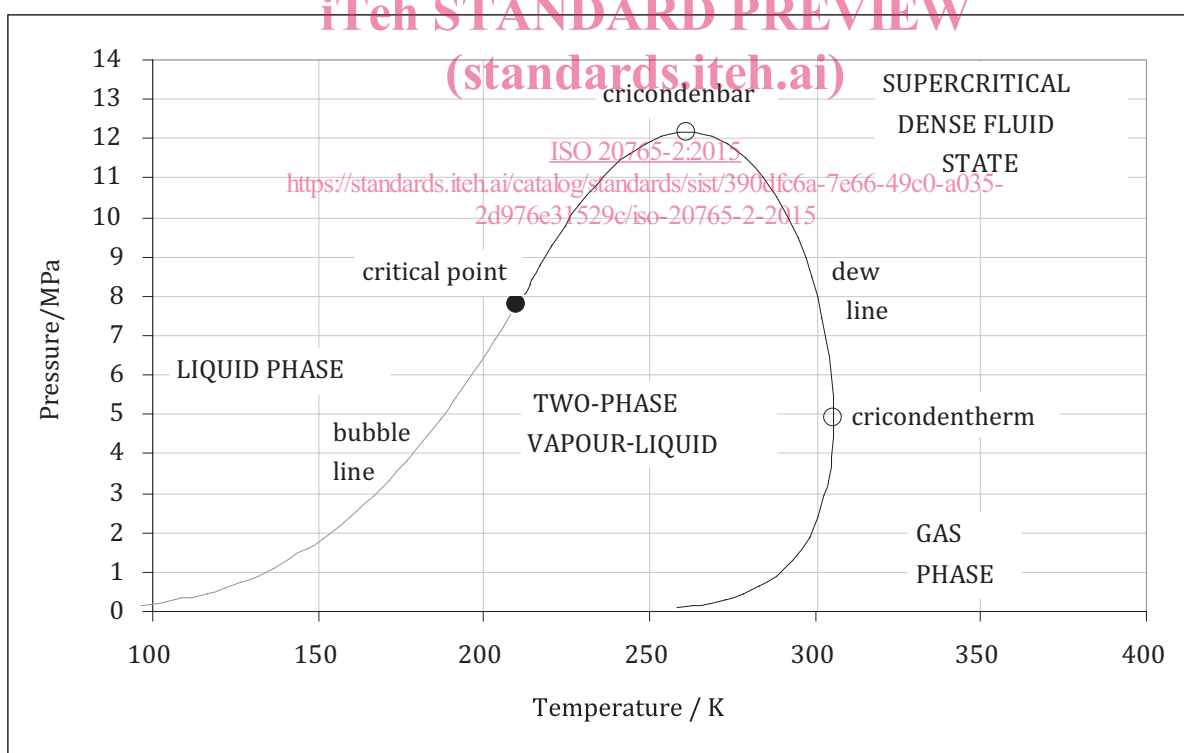


Figure 1 — Phase diagram for a typical natural gas

3.1 bubble pressure

pressure at which an infinitesimal amount of vapour is in equilibrium with a bulk liquid for a specified temperature

3.2 bubble temperature

temperature at which an infinitesimal amount of vapour is in equilibrium with a bulk liquid for a specified pressure

Note 1 to entry: The locus of bubble points is known as the bubble line.

Note 2 to entry: More than one bubble temperature may exist at a specific pressure. Moreover, more than one bubble pressure may exist at a specified temperature, as explained in the example given in [3.6](#).

3.3 cricondenbar

maximum pressure at which two-phase separation can occur

3.4 cricodentherm

maximum temperature at which two-phase separation can occur

3.5 critical point

unique saturation point along the two-phase vapour-liquid equilibrium boundary where both the vapour and liquid phases have the same composition and density

Note 1 to entry: The critical point is the point at which the dew line and the bubble line meet.

Note 2 to entry: The pressure at the critical point is known as the critical pressure and the temperature as the critical temperature.

Note 3 to entry: A mixture of given composition may have one, more than one, or no critical points. In addition, the phase behaviour may be quite different from that shown in [Fig. 1](#) for mixtures (including natural gases) containing, e.g., hydrogen or helium.

ISO 20765-2:2015

3.6 dew pressure

<https://standards.iteh.ai/catalog/standards/sist/390dfc6a-7e66-49c0-a035-2d976e31529c/iso-20765-2-2015>

pressure at which an infinitesimal amount of liquid is in equilibrium with a bulk vapour for a specified temperature

Note 1 to entry: More than one dew pressure may exist at the specified temperature. For example, isothermal compression at 300 K with a gas similar to that shown in [Figure 1](#): At low pressure the mixture is a gas. At just above 2 MPa (the dew pressure), a liquid phase initially forms. As pressure increases more liquid forms in the two-phase region, but a further increase in pressure reduces the amount of liquid (retrograde condensation) until at about 8 MPa where the liquid phase disappears at the upper dew pressure, and the mixture is in the dense gas phase. In the two-phase region, the overall composition is as specified, however the coexisting vapour and liquid will have different compositions.

3.7 dew temperature

temperature at which an infinitesimal amount of liquid is in equilibrium with a bulk vapour for a specified pressure

Note 1 to entry: More than one dew temperature may exist at a specified pressure, similar to the example given in [3.6](#).

Note 2 to entry: The locus of dew points is known as the dew line.

3.8 supercritical state

dense phase region above the critical point (often considered to be a state above the critical temperature and pressure) within which no two-phase separation can occur

4 Thermodynamic basis of the method

4.1 Principle

The method is based on the concept that natural gas or any other type of mixture can be completely characterized in 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 calculation of properties. In practice, the state variables available as input data are generally temperature and pressure, and it is thus necessary to first iteratively determine the density using the equations provided here.

These equations express the Helmholtz free energy of the mixture as a function of density, temperature, and composition, from which all other thermodynamic properties in the homogeneous (single-phase) gas, liquid, and supercritical (dense-fluid) regions may be obtained in terms of the Helmholtz free energy and its derivatives with respect to temperature and density. For example, pressure is proportional to the first derivative of the Helmholtz energy with respect to density (at constant temperature).

NOTE These equations are also applicable in the calculation of two-phase properties (vapour-liquid equilibria). Additional composition-dependent derivatives are required and are presented in Part 3 of this International Standard.

The method uses a detailed molar composition analysis in which all components present in amounts exceeding 0,000 05 mole fraction (50 ppm) are specified. 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 C₆ and higher may be lumped together by molar mass and treated collectively as the normal isomer.

For some fluids, additional components such as C₉, C₁₀, water, and hydrogen sulfide may be present and need to be taken into consideration. For manufactured gases, hydrogen, carbon monoxide, and oxygen may also be present in the mixture.

More precisely, the method uses a 21-component analysis in which all of the major and most of the minor components of natural gas are included (see [Clause 6](#)). Any trace component present but not identified as one of the 21 specified components may be assigned appropriately to one of these 21 components (see [Annex F](#)).

4.2 The fundamental equation based on the Helmholtz free energy

4.2.1 Background

The GERG-2008 equation^[1] was published by the Lehrstuhl für Thermodynamik at the Ruhr-Universität Bochum in Germany as a new wide-range equation of state for the volumetric and caloric properties of natural gases and other mixtures. It was originally published in 2007^[2] and later updated in 2008.^[1] The new equation improves upon the performance of the AGA-8 equation^[3] for gas phase properties and in addition is applicable to the properties of the liquid phase, to the dense-fluid phase, to the vapour-liquid phase boundary, and to properties for two-phase states. The ranges of temperature, pressure, and composition to which the GERG-2008 equation of state applies are much wider than the AGA-8 equation and cover an extended range of application. The Groupe Européen de Recherches Gazières (GERG) supported the development of this equation of state over several years.

The GERG-2008 equation is explicit in the Helmholtz free energy, a formulation that enables all thermodynamic properties to be expressed analytically as functions of the free energy and of its derivatives with respect to the state conditions of temperature and density. There is generally no need for numerical differentiation or integration within any computer program that implements the method.

4.2.2 The Helmholtz free energy

The Helmholtz free energy a of a fluid mixture at a given mixture density ρ , temperature T , and molar composition \bar{x} can be expressed as the sum of a^0 describing the ideal gas behaviour and a^r describing the residual or real-gas contribution, as follows:

$$a(\rho, T, \bar{x}) = a^0(\rho, T, \bar{x}) + a^r(\rho, T, \bar{x}) \quad (1)$$

4.2.3 The reduced Helmholtz free energy

The Helmholtz free energy is often used in its dimensionless form $\alpha = a/(RT)$ as

$$\alpha(\delta, \tau, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}) \quad (2)$$

In this equation, the reduced (dimensionless) mixture density δ is given by

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \quad (3)$$

and the inverse reduced (dimensionless) mixture temperature τ is given by

$$\tau = \frac{T_r(\bar{x})}{T} \quad (4)$$

where

ρ_r and T_r are reducing functions for the mixture density and mixture temperature (see 4.2.7) depending on the molar composition of the mixture only.

The residual part α^r of the reduced Helmholtz free energy is given by

$$\alpha^r(\delta, \tau, \bar{x}) = \alpha_0^r(\delta, \tau, \bar{x}) + \Delta\alpha^r(\delta, \tau, \bar{x}) \quad (5)$$

In this equation, the first term on the right-hand side α_0^r describes the contribution of the residual parts of the reduced Helmholtz free energy of the pure substance equations of state, which are multiplied by the mole fraction of the corresponding substance, and calculated at the reduced mixture variables δ and τ (see equation (8)). The second term $\Delta\alpha^r$ is the departure function, which is the double summation over all binary specific and generalized departure functions developed for the respective binary mixtures (see equation (10)).

4.2.4 The reduced Helmholtz free energy of the ideal gas

The reduced Helmholtz free energy α^o represents the properties of the ideal-gas mixture at a given mixture density ρ , temperature T , and molar composition \bar{x} according to

$$\alpha^o(\rho, T, \bar{x}) = \sum_{i=1}^N x_i [\alpha_{oi}^o(\rho, T) + \ln x_i] \quad (6)$$

In this equation, the term $\sum x_i \ln x_i$ is the contribution from the entropy of mixing, and $\alpha_{oi}^o(\rho, T)$ is the dimensionless form of the Helmholtz free energy in the ideal-gas state of component i , as given by

$$\alpha_{oi}^o(\rho, T) = \ln \left(\frac{\rho}{\rho_{c,i}} \right) + \frac{R^*}{R} \left[n_{oi,1}^o + n_{oi,2}^o \frac{T_{c,i}}{T} + n_{oi,3}^o \ln \left(\frac{T_{c,i}}{T} \right) + \sum_{k=4,6} n_{oi,k}^o \ln \left| \sinh \left(g_{oi,k}^o \frac{T_{c,i}}{T} \right) \right| \right. \\ \left. - \sum_{k=5,7} n_{oi,k}^o \ln \left| \cosh \left(g_{oi,k}^o \frac{T_{c,i}}{T} \right) \right| \right] \quad (7)$$

where

$\rho_{c,i}$ and $T_{c,i}$ are the critical parameters of the pure components (see [Annex C](#)).

The values of the coefficients $n_{oi,k}^o$ and the parameters $g_{oi,k}^o$ for all 21 components are given in [Annex B](#).

NOTE 1 The method prescribed is taken without change from the method prescribed in Part 1 of this International Standard. The user should however be aware of significant differences that result inevitably from the change in definition of the inverse reduced temperature τ between Part 1 and Part 2.

NOTE 2 $R = 8,314\,472\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was the internationally accepted standard for the molar gas constant^[4] at the time of development of the equation of state. Equation (7) results from the integration of the equations for the ideal-gas heat capacities taken from [5], where a different molar gas constant was used than the one adopted in the mixture model presented here. The ratio R^*/R with $R^* = 8,314\,51\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ takes into account this difference and therefore leads to the exact solution of the original equations for the ideal-gas heat capacity.

4.2.5 The pure substance contribution to the residual part of the reduced Helmholtz free energy

The contribution of the residual parts of the reduced Helmholtz free energy of the pure substance equations of state α_o^r to the residual part of the reduced Helmholtz free energy of the mixture is

$$\alpha_o^r(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \alpha_{oi}^r(\delta, \tau) \quad (8)$$

where

$\alpha_{oi}^r(\delta, \tau)$ is the residual part of the reduced Helmholtz free energy of component i (i.e., the residual part of the respective pure substance equation of state listed in Table 2) and is given by

$$\alpha_{oi}^r(\delta, \tau) = \sum_{k=1}^{K_{\text{Pol},i}} n_{oi,k} \delta^{d_{oi,k}} \tau^{t_{oi,k}} + \sum_{k=K_{\text{Pol},i}+1}^{K_{\text{Pol},i}+K_{\text{Exp},i}} n_{oi,k} \delta^{d_{oi,k}} \tau^{t_{oi,k}} e^{-\delta^{c_{oi,k}}} \quad (9)$$

The equations for α_{oi}^r use the same basic structure as further detailed in Annex D.2. The values of the coefficients $n_{oi,k}$ and the exponents $d_{oi,k}$, $t_{oi,k}$ and $c_{oi,k}$ for all 21 components are given in Annex D.2.2.

4.2.6 The departure function contribution to the residual part of the reduced Helmholtz free energy

The purpose of the departure function is to further improve the accuracy of the mixture model in the description of thermodynamic properties in addition to fitting the parameters of the reducing functions (see 4.2.7) when sufficiently accurate experimental data are available to characterize the properties of the mixture. The departure function $\Delta\alpha^r$ of the multi-component mixture is the double summation over all binary specific and generalized departure functions developed for the binary subsystems and is given by

$$\Delta\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \Delta\alpha_{ij}^r(\delta, \tau, \bar{x}) \quad (10)$$

with

$$\Delta\alpha_{ij}^r(\delta, \tau, \bar{x}) = x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau) \quad (11)$$

In this equation, the function $\alpha_{ij}^r(\delta, \tau)$ is the part of the departure function $\Delta\alpha_{ij}^r(\delta, \tau, \bar{x})$ that depends only on the reduced mixture variables δ and τ , as given by

$$\alpha_{ij}^r(\delta, \tau) = \sum_{k=1}^{K_{\text{Pol},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{\text{Pol},ij}+1}^{K_{\text{Pol},ij}+K_{\text{Exp},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^2 - \beta_{ij,k}(\delta-\gamma_{ij,k})} \quad (12)$$

where

$\alpha_{ij}^r(\delta, \tau)$ was developed either for a specific binary mixture (a binary specific departure function with binary specific coefficients and exponents) or for a group of binary mixtures (generalized departure function with a uniform structure for the group of binary mixtures).

a) Binary specific departure functions

Binary specific departure functions were developed for the binary mixtures of methane with nitrogen, carbon dioxide, ethane, propane, and hydrogen, and of nitrogen with carbon dioxide and ethane. For a binary specific departure function, the adjustable factor F_{ij} in equation (11) equals unity.

b) Generalized departure function

A generalized departure function was developed for the binary mixtures of methane with n-butane and isobutane, of ethane with propane, n-butane, and isobutane, of propane with n-butane and isobutane, and of n-butane with isobutane. For each mixture in the group of generalized binary mixtures, the

parameter F_{ij} is fitted to the corresponding binary specific data (except for the binary system methane-n-butane, where F_{ij} equals unity).

c) **No departure function**

For all of the remaining binary mixtures, no departure function was developed, and F_{ij} equals zero, i.e., $\Delta\alpha_{ij}^r(\delta, \tau, \bar{x})$ equals zero. For most of these mixtures, however, the parameters of the reducing functions for density and temperature were fitted to selected experimental data (see 4.2.7 and 6.2).

The values of the coefficients $n_{ij,k}$, the exponents $d_{ij,k}$ and $t_{ij,k}$, and the parameters $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ for all binary specific and generalized departure functions considered in the mixture model described here are given in Annex D.3, Table D.4. The number of digits given in these tables is as presented in the source publication; the effect of truncation is not obvious and all of the digits shall be used in all calculations. The non-zero F_{ij} parameters are listed in Table D.5.

NOTE Compared to the reducing functions for density and temperature, the departure function is in general of minor importance for the residual behaviour of the mixture since it only describes an additional small residual deviation to the real mixture behaviour. The development of such a function was, however, necessary to fulfil the high demands on the accuracy of the mixture model presented here in the description of the thermodynamic properties of natural gases and other mixtures.

4.2.7 Reducing functions

The reduced mixture variables δ and τ are calculated from equations (3) and (4) by means of the composition-dependent reducing functions for the mixture density and temperature

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \left[\frac{1}{8} \right] \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \tag{13}$$

$$T_r(\bar{x}) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \frac{20(T_{c,i} + T_{c,j})}{T_{c,i} + T_{c,j}} \tag{14}$$

These functions are based on quadratic mixing rules and are reasonably connected to physically well-founded mixing rules. The binary parameters $\beta_{v,ij}$ and $\gamma_{v,ij}$ in equation (13) and $\beta_{T,ij}$ and $\gamma_{T,ij}$ in equation (14) are fitted to data for binary mixtures subject to the conditions $\beta_{ij}=1/\beta_{ji}$ and $\gamma_{ij}=\gamma_{ji}$. The values of the binary parameters for all binary mixtures are listed in Table E.1 of Annex E. The critical parameters $\rho_{c,i}$ and $T_{c,i}$ of the pure components are given in Annex C.

NOTE The binary parameters of equations (13) and (14) were fitted based on the deviations between the behaviour of the real mixture (determined by experimental data) and the one resulting from ideal combining rules (with β and γ set to 1) for the critical parameters of the pure components. In those cases where sufficient experimental data are not available, the parameters of equations (13) and (14) are either set to unity or modified (calculated) in such a manner that the critical parameters of the pure components are combined in a different way, which proved to be more suitable for certain binary subsystems (see also Annex E.1).

4.3 Thermodynamic properties derived from the Helmholtz free energy

4.3.1 Background

The thermodynamic properties in the homogeneous gas, liquid, and supercritical regions of a mixture are related to derivatives of the Helmholtz free energy with respect to the reduced mixture variables δ and τ , as summarized in the following section (see Table 1). All of the thermodynamic properties may

be written explicitly in terms of the reduced Helmholtz free energy α and its various derivatives. The required derivatives α_τ , $\alpha_{\tau\tau}$, α_δ , $\alpha_{\delta\delta}$, and $\alpha_{\delta\tau}$ are defined as follows:

$$\alpha_\tau = \left(\frac{\partial \alpha}{\partial \tau} \right)_{\delta, \bar{x}} \quad \alpha_{\tau\tau} = \left(\frac{\partial^2 \alpha}{\partial \tau^2} \right)_{\delta, \bar{x}} \quad \alpha_\delta = \left(\frac{\partial \alpha}{\partial \delta} \right)_{\tau, \bar{x}} \quad \alpha_{\delta\delta} = \left(\frac{\partial^2 \alpha}{\partial \delta^2} \right)_{\tau, \bar{x}} \quad \alpha_{\delta\tau} = \left(\frac{\partial}{\partial \tau} \left(\frac{\partial \alpha}{\partial \delta} \right)_{\tau, \bar{x}} \right)_{\delta, \bar{x}} \quad (15)$$

Each derivative is the sum of an ideal-gas part (see [Annex B](#)) and a residual part (see [Annex D](#)). The following substitutions help to simplify the appearance of the relevant relationships:

$$\alpha_1 = \left(\frac{\partial(\delta^2 \alpha_\delta)}{\partial \delta} \right)_{\tau, x_i} = 2\delta \alpha_\delta + \delta^2 \alpha_{\delta\delta} = 1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r \quad (16)$$

$$\alpha_2 = -\tau^2 \left(\frac{\partial}{\partial \tau} \left(\frac{\delta \alpha_\delta}{\tau} \right) \right)_{\delta, x_i} = \delta \alpha_\delta - \delta \tau \alpha_{\delta\tau} = 1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta\tau}^r \quad (17)$$

Detailed expressions for α_τ , $\alpha_{\tau\tau}$, α_δ , $\alpha_{\delta\delta}$, $\alpha_{\delta\tau}$, α_1 , and α_2 can be found in [Annexes B](#) and [D](#).

NOTE In addition to the derivatives of α with respect to the reduced mixture variables δ and τ , composition derivatives of α and of the reducing functions for density and temperature are required for the calculation of vapour-liquid equilibrium (VLE) properties as described in Part 3 of this International Standard.

4.3.2 Relations for the calculation of thermodynamic properties in the homogeneous region

The relations between common thermodynamic properties and the reduced Helmholtz free energy α and its derivatives are summarized in [Table 1](#). The first column of this table defines the thermodynamic properties. The second column gives their relation to the reduced Helmholtz free energy α of the mixture. In equations (26), (28), (29), (30), and (31), the basic expressions for the properties c_p , w , μ_{JT} , ϕ , and κ have been additionally transformed, 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.

In equations (22) to (27), the relations for the thermodynamic properties represent the molar quantities (i.e., quantity per mole, lower case symbols). Specific quantities (i.e., quantity per kilogram, represented normally by upper case symbols) are obtained by dividing the molar variables (e.g., v , u , s , h , g , c_v , and c_p) by the molar mass M .

The molar mass M of the mixture is derived from the composition x_i and the molar masses M_i of the pure substances, as follows

$$M(\bar{x}) = \sum_{i=1}^N x_i \cdot M_i \quad (18)$$

The mass-based density D is given by

$$D = \rho M \quad (19)$$

NOTE 1 Values of the molar masses M_i of the pure substances are given in [Annex C](#) and are taken from [6]; these values are not identical with those given in ISO 20765-1 and ISO 6976:1995.[7] However, they are identical with the most recent values adopted by the international community of metrologists. In these equations, R is the molar gas constant; consequently R/M is the specific gas constant.

NOTE 2 See [Annex B.1](#) for information on reference states for enthalpy and entropy.