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Natural gas — Calculation of thermodynamic properties —

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

Gaz naturel — Calcul des propriétés thermodynamiques —

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

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Contents

Foreword

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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)*

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 ≤ 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 CO_2 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 ≤(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 ±(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.

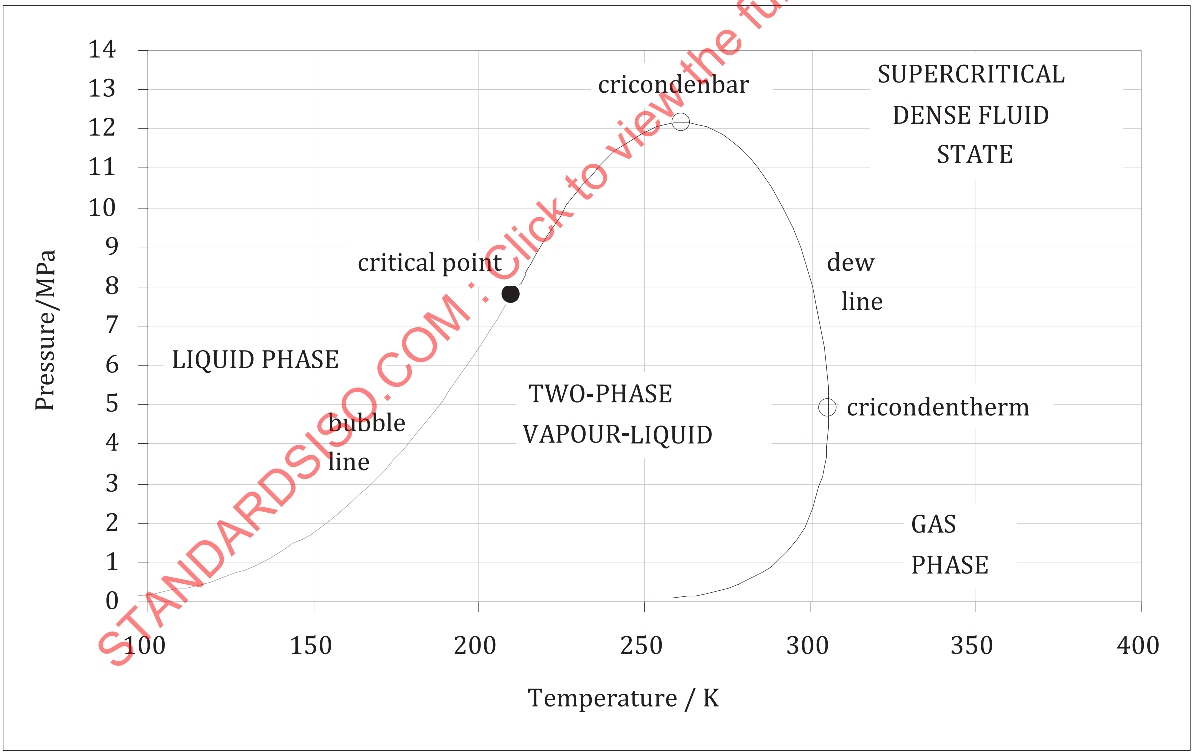

Figure 1 — Phase diagram for a typical natural gas

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
cricondentherm
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.

3.6
dew pressure
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 C_7 or C_8 together with nitrogen, carbon dioxide, and helium. Typically, isomers for alkanes C_6 and higher may be lumped together by molar mass and treated collectively as the normal isomer.

For some fluids, additional components such as C_9, C_{10}, 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^{o} describing the ideal gas behaviour and a^{r} describing the residual or real-gas contribution, as follows:

$$a(\rho,T,\bar{x})=a^{\mathrm{o}}(\rho,T,\bar{x})+a^{\mathrm{r}}(\rho,T,\bar{x}) \tag{1}$$

4.2.3 The reduced Helmholtz free energy

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

$$\alpha(\delta,\tau,\bar{x})=\alpha^{\mathrm{o}}(\rho,T,\bar{x})+\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{2}$$

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

$$\delta=\frac{\rho}{\rho_{\mathrm{r}}(\bar{x})} \tag{3}$$

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

$$\tau=\frac{T_{\mathrm{r}}(\bar{x})}{T} \tag{4}$$

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

$$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})=\alpha_{\mathrm{o}}^{\mathrm{r}}(\delta,\tau,\bar{x})+\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{5}$$

In this equation, the first term on the right-hand side $\alpha_{\mathrm{o}}^{\mathrm{r}}$ 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 $\Delta\alpha^{\mathrm{r}}$ 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

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

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

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

where

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

The values of the coefficients $n_{\mathrm{o}i,k}^{\mathrm{o}}$ and the parameters $\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}$ 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 $R = 8{,}314\,472\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ 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 $R^*=8{,}314\,51\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ 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 $\alpha_{\mathrm{o}}^{\mathrm{r}}$ to the residual part of the reduced Helmholtz free energy of the mixture is

$$\alpha_{\mathrm{o}}^{\mathrm{r}}(\delta,\tau,\bar{x})=\sum_{i=1}^{N}x_i\,\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) \tag{8}$$

where

$\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$ 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

$$\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)=\sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}}+\sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}}\,e^{-\delta^{c_{\mathrm{o}i,k}}} \tag{9}$$

The equations for $\alpha^{\mathrm{r}}_{\mathrm{o}i}$ use the same basic structure as further detailed in Annex D.2. The values of the coefficients $n_{\mathrm{o}i,k}$ and the exponents $d_{\mathrm{o}i,k}$, $t_{\mathrm{o}i,k}$ and $c_{\mathrm{o}i,k}$ 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 $\Delta\alpha^{\mathrm{r}}$ 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

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

with

$$\Delta\alpha^{\mathrm{r}}_{ij}(\delta,\tau,\bar{x})=x_i x_j F_{ij}\,\alpha^{\mathrm{r}}_{ij}(\delta,\tau) \tag{11}$$

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

$$\begin{aligned}\alpha^{\mathrm{r}}_{ij}(\delta,\tau)={}&\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\\&+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^{2}-\beta_{ij,k}(\delta-\gamma_{ij,k})}\end{aligned} \tag{12}$$

where

$\alpha^{\mathrm{r}}_{ij}(\delta,\tau)$ 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., $\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x})$ 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

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

$$T_{\mathrm{r}}(\bar{x})=\sum_{i=1}^{N}\sum_{j=1}^{N}x_i x_j\,\beta_{T,ij}\,\gamma_{T,ij}\,\frac{x_i+x_j}{\beta_{T,ij}^{2}\,x_i+x_j}\left(T_{\mathrm{c},i}\cdot T_{\mathrm{c},j}\right)^{0.5} \qquad (14)$$

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:

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

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:

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

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

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

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

The mass-based density D is given by

$$D=\rho M \tag{19}$$

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.

Table 1 — Definitions of common thermodynamic properties and their relation to the reduced Helmholtz free energy *α*

Property and definition	Relation to *α* and its derivatives	
Pressure $p=-(\partial a/\partial v)_{T,\bar{x}}$	$\dfrac{p}{\rho RT}=1+\delta\alpha_{\delta}^{\mathrm{r}}$	(20)
Compression factor $Z=p/(\rho RT)$	$Z=1+\delta\alpha_{\delta}^{\mathrm{r}}$	(21)
Internal energy $u=a+Ts$	$\dfrac{u}{RT}=\tau\alpha_{\tau}$	(22)
Entropy $s=-(\partial a/\partial T)_{v,\bar{x}}$	$\dfrac{s}{R}=\tau\alpha_{\tau}-\alpha$	(23)
Isochoric heat capacity $c_v=(\partial u/\partial T)_{v,\bar{x}}$	$\dfrac{c_v}{R}=-\tau^2\alpha_{\tau\tau}$	(24)
Enthalpy $h=u+pv$	$\dfrac{h}{RT}=1+\delta\alpha_{\delta}^{\mathrm{r}}+\tau\alpha_{\tau}$	(25)
Isobaric heat capacity $c_p=(\partial h/\partial T)_{p,\bar{x}}$	$\dfrac{c_p}{R}=-\tau^2\alpha_{\tau\tau}+\dfrac{\alpha_2^2}{\alpha_1}$	(26)
Gibbs free energy $g=h-Ts$	$\dfrac{g}{RT}=1+\delta\alpha_{\delta}^{\mathrm{r}}+\alpha$	(27)
Speed of sound $w^2=(1/M)(\partial p/\partial\rho)_{s,\bar{x}}$	$\dfrac{w^2M}{RT}=\alpha_1-\dfrac{\alpha_2^2}{\tau^2\alpha_{\tau\tau}}=Z\kappa=\alpha_1\dfrac{c_p}{c_v}$	(28)
Joule-Thomson coefficient $\mu=(\partial T/\partial p)_{h,\bar{x}}$	$\mu R\rho=\dfrac{\alpha_2-\alpha_1}{\alpha_2^2-\tau^2\alpha_{\tau\tau}\alpha_1}=\dfrac{R}{c_p}\left(\dfrac{\alpha_2}{\alpha_1}-1\right)$	(29)
Isothermal throttling coefficient $\phi=(\partial h/\partial p)_{T,\bar{x}}$	$\phi\rho=1-\dfrac{\alpha_2}{\alpha_1}$	(30)
Isentropic exponent $\kappa=-(v/p)(\partial p/\partial v)_{s,\bar{x}}$	$\kappa=\dfrac{\alpha_1}{1+\delta\alpha_{\delta}^{\mathrm{r}}}\left(1-\dfrac{\alpha_2^2}{\tau^2\alpha_{\tau\tau}\alpha_1}\right)=\dfrac{\alpha_1}{Z}\dfrac{c_p}{c_v}$	(31)
Second virial coefficient $B=\lim\limits_{\rho\to 0}(\partial Z/\partial\rho)_{T,\bar{x}}$	$B\rho_{\mathrm{r}}=\lim\limits_{\delta\to 0}(\alpha_{\delta}^{\mathrm{r}})$	(32)
Third virial coefficient $C=\lim\limits_{\rho\to 0}(\partial^2Z/\partial\rho^2)_{T,\bar{x}}/2$	$C\rho_{\mathrm{r}}^2=\lim\limits_{\delta\to 0}(\alpha_{\delta\delta}^{\mathrm{r}})$	(33)

5 Method of calculation

5.1 Input variables

The method presented in this standard uses reduced density, inverse reduced temperature, and molar composition as the input variables. If the mass-based density D is available as input, then ρ is obtained directly as $\rho = D/M$, where $M(\bar{x})$ is the molar mass given by equation (18). For given values of the molar density ρ, temperature T, and molar composition $\bar{x}$, the reduced mixture variables δ and τ can be calculated from equations (3) and (4) using the reducing functions for density and temperature given by equations (13) and (14).

More often, however, absolute pressure, temperature, and molar composition are available as the input variables. As a consequence, it is usually necessary to first evaluate the reduced density δ and the inverse reduced temperature τ from the available inputs. The conversion from temperature to inverse reduced temperature is given by equation (4). Section 5.2 explains how to obtain the reduced density given pressure and temperature.

The composition in mole fractions is required for the following 21 components: methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane (2-methylpropane), n-pentane, isopentane (2-methylbutane), n-hexane, n-heptane, n-octane, n-nonane, n-decane, hydrogen, oxygen, carbon monoxide, water, hydrogen sulfide, helium, and argon. For natural gases and similar (multi-component) mixtures, the allowable ranges of mole fraction are defined in 6.3. The sum of all mole fractions shall be unity.

NOTE 1 If the sum of all mole fractions is not unity within the limit of analytical resolution, then the composition is either faulty or incomplete. The user should not proceed until the source of this problem has been identified and eliminated.

NOTE 2 If the mole fractions of heptanes, octanes, nonanes, and decanes are unknown, then the use of a composite C6+ fraction may be applicable for density calculation, where the composite components are split into individual fractions. VLE calculations (including dew points) obtain the best results when all components in the mixture are quantified. The composite component simplification (C6+) may have a higher uncertainty since even small amounts of heptanes, octanes, nonanes, decanes, and higher hydrocarbons have a significant influence on the phase behaviour of the mixture. The user should carry out a sensitivity analysis in order to test whether a particular approximation of this type is suitable for the intended purpose.

NOTE 3 Composition given in volume or mass fractions will need to be converted to mole fractions using the method given in ISO 14912.[8]

5.2 Conversion from pressure to reduced density

The combination of the relations for the reduced mixture variables δ and τ (equations (3) and (4)) and equation (21) results in the following expression

$$\frac{p\tau}{\delta\,\rho_{\mathrm{r}}(\bar{x})RT_{\mathrm{r}}(\bar{x})} = Z(\delta,\tau,\bar{x}) = 1 + \delta\,\alpha^{\mathrm{r}}_{\delta}(\delta,\tau,\bar{x}) \tag{34}$$

where

$$\alpha^{\mathrm{r}}_{\delta}(\delta,\tau,\bar{x}) = \left(\frac{\partial\alpha^{\mathrm{r}}}{\partial\delta}\right)_{\tau,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)}{\partial\delta}\right)_{\tau} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial\alpha^{\mathrm{r}}_{ij}(\delta,\tau)}{\partial\delta}\right)_{\tau} \tag{35}$$

If the input variables are available as pressure, temperature, and molar composition, equation (34) may be solved for the reduced molar density δ. The derivatives of $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$ with respect to δ and the coefficients and exponents involved (see equation (9)) are given in Annex D.2. The derivatives of $\alpha^{\mathrm{r}}_{ij}(\delta,\tau)$ with respect to δ and the coefficients and exponents involved (see equations (11) and (12)) are given in Annex D.3. Information on the reducing functions is given in Annex E.

The solution of equation (34) requires any suitable numerical method, where, in practice, a standard form of equation-of-state density-search algorithm may be the most convenient and satisfactory. Such algorithms usually use an initial estimate of the density (e.g., the ideal-gas approximation for low density gaseous states) and proceed to calculate the pressure p. In an iterative procedure, density values are changed with decreasing increments to find the optimal density that reproduces the known value of pressure to within a pre-established level of agreement. A suitable criterion in the present case is that the pressure p calculated from the iteratively determined reduced density δ shall reproduce the input value of p at least to within 1 part in 10^6. The user must be careful to determine that the calculated state is stable since multiple roots can exist.

5.3 Implementation

Once the independent variables reduced density δ, inverse reduced temperature τ, and molar composition $\bar{x}$ of the mixture are known, the reduced Helmholtz free energy and the other thermodynamic properties (see Table 1) can be calculated. Equation (2) formulates the reduced Helmholtz free energy as $\alpha=\alpha^{o}+\alpha^{r}$. The relations for the ideal-gas part α^{o} are given in equations (6) and (7). The relations for the residual part α^{r}, which is formulated as a function of the reduced density δ, the inverse reduced temperature τ, and the molar composition $\bar{x}$, are specified in equations (5) and (8) to (12) so as to give the following expression for α:

$$\begin{aligned}\alpha(\delta,\tau,\bar{x}) = {} & \sum_{i=1}^{N} x_i \frac{R^*}{R}\left[n_{\mathrm{oi},1}^{\mathrm{o}} + n_{\mathrm{oi},2}^{\mathrm{o}} \frac{T_{\mathrm{c},i}}{T} + n_{\mathrm{oi},3}^{\mathrm{o}} \ln\left(\frac{T_{\mathrm{c},i}}{T}\right) + \sum_{k=4,6} n_{\mathrm{oi},k}^{\mathrm{o}} \ln\left|\sinh\left(\vartheta_{\mathrm{oi},k}^{\mathrm{o}} \frac{T_{\mathrm{c},i}}{T}\right)\right|\right. \\ & \left. - \sum_{k=5,7} n_{\mathrm{oi},k}^{\mathrm{o}} \ln\left|\cosh\left(\vartheta_{\mathrm{oi},k}^{\mathrm{o}} \frac{T_{\mathrm{c},i}}{T}\right)\right|\right] + \sum_{i=1}^{N} x_i \left[\ln\left(\frac{\rho}{\rho_{\mathrm{c},i}}\right) + \ln x_i\right] \\ & + \sum_{i=1}^{N} x_i \left[\sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{oi},k}\, \delta^{d_{\mathrm{oi},k}} \tau^{t_{\mathrm{oi},k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{oi},k}\, \delta^{d_{\mathrm{oi},k}} \tau^{t_{\mathrm{oi},k}} e^{-\delta^{c_{\mathrm{oi},k}}}\right] \\ & + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left[\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\, \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\, \delta^{d_{ij,k}} \tau^{t_{ij,k}} e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^2-\beta_{ij,k}(\delta-\gamma_{ij,k})}\right]\end{aligned} \tag{36}$$

For all 21 components, the values of the coefficients $n_{\mathrm{oi},k}^{\mathrm{o}}$ and the parameters $\vartheta_{\mathrm{oi},k}^{\mathrm{o}}$ of the ideal-gas part of the reduced Helmholtz free energy are given in Annex B. The values of the coefficients $n_{\mathrm{oi},k}$ and exponents $d_{\mathrm{oi},k}$, $t_{\mathrm{oi},k}$, and $c_{\mathrm{oi},k}$ in the contribution to the residual parts of the pure substance equations of state are listed in Annex D. The values of the coefficients $n_{ij,k}$, the exponents $d_{ij,k}$ and $t_{ij,k}$, and the parameters F_{ij}, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ in the departure functions for all relevant binary mixtures are given in Annex D.

Derivatives of α with respect to the reduced mixture variables δ and τ that are needed for the calculation of the various thermodynamic properties may be obtained from Annexes B and D. Annex B lists the derivatives of the ideal-gas part of the reduced Helmholtz free energy, a^{o}, with respect to the reduced density and inverse reduced temperature of the mixture. Derivatives of the contribution of the residual parts of the pure substance equations of state to the reduced residual Helmholtz free energy of the mixture, a^{r}, with respect to the reduced mixture variables δ and τ may be obtained from Annex D. Derivatives of the contribution of the departure functions for binary mixtures to a^{r} with respect to the reduced mixture variables δ and τ are also given in Annex D.

6 Ranges of application

6.1 Pure gases

The temperature and pressure ranges of validity for the pure fluid equations of state are listed in Table 2. For these ranges, the equations have been verified by experimental data. The lower temperatures correspond to rounded values of the triple point temperatures of the substances. For the main components, the equations are valid for temperatures up to at least 600 K (620 °F) and pressures from a perfect vacuum state up to 300 MPa (43 500 psia). For the secondary alkanes, the equations are valid for temperatures up to at least 500 K (440 °F) and pressures up to at least 35 MPa (5075 psia). For the other secondary components, the temperatures range up to at least 400 K (260 °F) (water up to 1273 K, 1830 °F) and pressures range up to at least 100 MPa (14 500 psia). The extrapolation yields reasonable results at temperatures and pressures far beyond the listed (tested) ranges of validity.

Table 2 — Validity range and references for the 21 components in the mixture model[a]

Pure substance	Reference	Tested range of validity		Number of terms
		Temperature	Pressure	
		T/K	$p_{\max}$/MPa	
Main components				
Methane	Klimeck (2000)[9]	90 – 623	300	24
Nitrogen	Klimeck (2000)[9]	63 – 700	300	24
Carbon dioxide	Klimeck (2000)[9]	90[b] – 900	300	22
Ethane	Klimeck (2000)[9]	90 – 623	300	24
Secondary alkanes				
Propane	Span & Wagner (2003)[10]	85 – 623	100	12
n-Butane	Span & Wagner (2003)[10]	134 – 693	70	12
Isobutane	Span & Wagner (2003)[10]	113 – 573	35	12
n-Pentane	Span & Wagner (2003)[10]	143 – 573	70	12
Isopentane	Lemmon & Span (2006)[11]	112 – 500	35	12
n-Hexane	Span & Wagner (2003)[10]	177 – 548	100	12
n-Heptane	Span & Wagner (2003)[10]	182 – 523	100	12
n-Octane	Span & Wagner (2003)[10]	216 – 548	100	12
n-Nonane	Lemmon & Span (2006)[11]	219 – 600	800	12
n-Decane	Lemmon & Span (2006)[11]	243 – 675	800	12
Other secondary components				
Hydrogen[c]	Kunz et al. (2007)[1]	14 – 700	300	14
Oxygen	Span & Wagner (2003)[10]	54 – 500[e]	100	12
Carbon monoxide	Lemmon & Span (2006)[11]	68 – 400	100	12
Water	Kunz et al. (2007)[1]	273 – 1 273	100	16
Hydrogen sulfide	Lemmon & Span (2006)[11]	187 – 760	170	12
Helium[d]	Kunz et al. (2007)[1]	2,2 – 573	100	12
Argon	Span & Wagner (2003)[10]	83 – 520	100	12

[a] The tabulated references document the equations for the residual part of the Helmholtz free energy of the pure substances. Equations for the isobaric heat capacity in the ideal-gas state taken from reference [5] were used to derive the Helmholtz free energy of the ideal gas for all components. Ranges listed are for volumetric properties only (density, compressibility factor, and vapour pressure). Components with a different lower limit for the ideal heat capacity than that listed in the table are: n-C_5, i-C_5, n-C_6 and n-C_7 (200 K), and H_2 and O_2 (100 K). See the publication of Jaeschke and Schley[5] for additional information on the limits of caloric properties.

[b] The equation can be extrapolated from the triple-point temperature of 216 K down to 90 K for the vapour phase.

[c] The equation given in Kunz et al.[1] represents equilibrium-hydrogen; volumetric properties of normal-hydrogen and para-hydrogen are nearly the same as those for e-hydrogen. The heat capacity equation for the ideal gas reported by Jaeschke and Schley[5] is for n-H2. The difference in heat capacities between e-H2 and n-H2 are significant below about 200 K.

[d] Represents helium-4. The lower temperature limit of the equation of state is the lambda point at which helium I transitions to helium II for the saturated liquid.

[e] The upper limit of the oxygen equation has been increased to 500 K based on recent validation.

6.2 Binary mixtures

Table 3 summarizes the available data for volumetric and caloric properties of all binary mixtures considered in this method. Almost half of the data come from the 15 mixtures with binary specific or generalized departure functions. The majority of the data (approximately 65 %) describe the *pρT* relation, approximately 25 % are vapour-liquid equilibrium state points, and about 9 % are caloric properties.

a) Specific departure functions

Table 4 lists the binary mixtures for which either binary specific or generalized departure functions were developed with sufficiently accurate and extensive data sets. Binary specific departure functions are available for the binary mixtures of methane with nitrogen, carbon dioxide, ethane, propane, and hydrogen, and of nitrogen with carbon dioxide and ethane (see also figure 2).

The experimental data used to test the equations developed for the binary mixtures cover a region from about 80 K (–315 °F) to 700 K (800 °F) at pressures up to 70 MPa (10150 psia) or more (e.g., 100 MPa (14500 psia) for methane–carbon dioxide and 750 MPa (110 000 psia) for methane–nitrogen). The data cover compositions from nearly 0 to 1 for all mixtures listed above; see [2] for further details.

b) Generalized departure function

A generalized departure function was developed for eight binary mixtures of secondary alkanes (see Table 4). The generalized departure function is used for the binary mixtures of methane with n-butane and isobutane, ethane with propane, n-butane, and isobutane, propane with n-butane and isobutane, and n-butane with isobutane.

In addition to the experimental data for these binary mixtures, selected volumetric and caloric properties for the well-measured mixtures methane–ethane and methane–propane were also used for the development of the generalized departure function. The final structure is mostly based on accurate and comprehensive data sets for the three binary systems methane–ethane, methane–propane, and methane–n-butane, with more than 6200 selected data points (about 1000 data points for the methane–n-butane binary system). The temperature range of the experimental data used to test the equations for the secondary binary alkane mixtures covers roughly 95 K to 600 K (–290 °F to 620 °F) at pressures up to 35 MPa (5075 psia) (70 MPa for methane–n-butane). The composition ranges from nearly 0 to 1 for all mixtures listed above; see [2] for further details.

c) No departure functions

No departure function was developed for the remaining binary mixtures (see Figure 2). These mixtures are either characterized by limited data, which do not permit the development of binary specific or generalized departure functions, or are of minor importance for the description of the thermodynamic properties of multi-component natural gases due to the small mole fractions of the respective components. Fitting the parameters of the reducing functions for density and temperature to selected experimental data is sufficient and yields good results for most of the binary mixtures. When sufficient experimental data are not available, the parameters of the reducing functions 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).

For the temperature, pressure, and composition ranges covered by the experimental data used to test the equations developed for the binary mixtures without a departure function, i.e., by adjusting the reducing functions for density and temperature only, see [2].

Table 3 — Summary of the available data for volumetric and caloric properties of binary mixtures

Data type	Number of data points	Temperature range	Pressure range	Composition range
		T/K	p/MPa	x
Density	51 442	66,9 – 800	0,00 – 1 027	0,00 – 1,00
Isochoric heat capacity	1 236	101 – 345	67,1[ρ] – 902[ρ]	0,01 – 0,84

[a] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary *pρT*.

[ρ] Density in kg·m^{-3} instead of pressure.

Table 3 *(continued)*

Data type	Number of data points	Temperature range	Pressure range	Composition range
		T/K	p/MPa	x
Density	51 442	66,9 – 800	0,00 – 1 027	0,00 – 1,00
Speed of sound	2 819	157 – 450	0,00 – 1 971	0,01 – 0,96
Isobaric heat capacity	1 072	100 – 424	0,00 – 52,9	0,09 – 0,93
Enthalpy differences	1 804	107 – 525	0,00 – 18,4	0,05 – 0,90
Excess molar enthalpy	177	221 – 373	0,8 – 15,0	0,01 – 0,98
Saturated liquid density[a]	460	95,0 – 394	0,03 – 22,1	0,00 – 1,00
VLE data	20 161	15,5 – 700	0,00 – 422	0,00 – 1,00
Total	79 171	15,5 – 800	0,00 – 1 971	0,00 – 1,00

[a] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$.

ρ Density in kg·m^{-3} instead of pressure.

Table 4 — Binary mixtures for which specific or generalized departure functions were developed

Binary mixture	Type of departure function	Number of terms	Type of terms[a]
Methane–Nitrogen	Binary specific	9	P (2), E (7)
Methane–Carbon dioxide	Binary specific	6	P (3), E (3)
Methane–Ethane	Binary specific	12	P (2), E (10)
Methane–Propane	Binary specific	9	P (5), E (4)
Methane–n-Butane	Generalized	10	P
Methane–Isobutane	Generalized	10	P
Methane–Hydrogen	Binary specific	4	P
Nitrogen–Carbon dioxide	Binary specific	6	P (2), E (4)
Nitrogen–Ethane	Binary specific	6	P (3), E (3)
Ethane–Propane	Generalized	10	P
Ethane–n-Butane	Generalized	10	P
Ethane–Isobutane	Generalized	10	P
Propane–n-Butane	Generalized	10	P
Propane–Isobutane	Generalized	10	P
n-Butane–Isobutane	Generalized	10	P

[a] “P” indicates polynomial terms, and “E” indicates terms composed of a polynomial and exponential expression according to equation (12). The numbers in parentheses indicate the respective number of terms Kpol and Kexp.

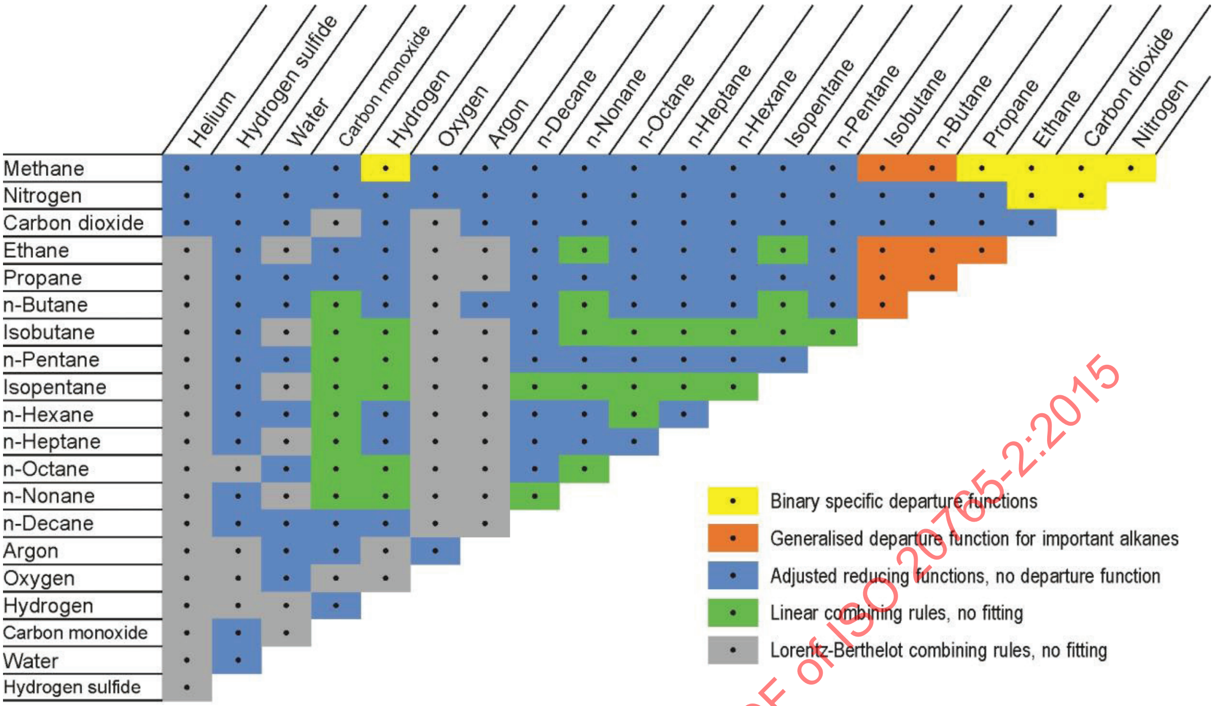

Figure 2 — Overview of the 210 binary combinations that result from the 21 natural gas components for the development of the GERG-2008 equation of state. The diagram shows the different formulations developed for the binary mixtures.

6.3 Natural gases

Table 5 — Ranges of application[a]

	Normal range	Full range
Pressure (absolute)	$0 < p$ / MPa ≤ 35	$0 < p$ / MPa ≤ 70
Temperature	$90 \leq T$ / K ≤ 450	$60 \leq T$ / K ≤ 700
Pressure (absolute)	$0 < p$ / psia ≤ 5075	$0 < p$ / psia ≤ 10150
Temperature	$-298 \leq T$ / °F ≤ 350	$-352 \leq T$ / °F ≤ 800

[a] Ranges listed are for volumetric properties only (density, compressibility factor, and vapour pressure). Other properties have a lower temperature limit of approximately 200 K. See the publication of Jaeschke and Schley[5] for additional information on the limits of the caloric equations.

Pipeline quality natural gas is generally described as a mixture of various components with mole fractions that fall within the ranges given in the third column of Table 6. The method described in ISO 20765-1 applies only to pipeline quality natural gases at temperatures and pressures found in transmission and distribution operations. The method given in this standard not only applies to these conditions but also to an intermediate composition range of natural gas as given in the fourth column of Table 6. Accurate and extensive experimental data sets are available within the composition ranges listed in the table and have been used to validate the quality of the method presented here (see 7.4). Possible trace components of natural gases, and details of how to deal with these, are discussed in Annex F. This method is not applicable where the total of all trace components exceeds 0,000 5 mole fraction.

Beyond the intermediate quality range is the full range that covers all compositions for all mixture components, i.e., from 0 to 1. Due to limited data, results obtained for multi-component mixtures in the full range of application should be carefully assessed. The method can also be used for temperatures above 700 K (800 °F) and pressures above 70 MPa (10150 psia); however, due to the limited data it is difficult to estimate the uncertainty of the method (see 7).

Table 6 — Mole fraction ranges for components of intermediate and pipeline quality natural gas

i	Component	Mole fractions for	
		Pipeline quality range	Intermediate quality range
1	Methane	$0,7 \le x_{CH4} \le 1,00$	$0,3 \le x_{CH4} \le 1,00$
2	Nitrogen	$0 \le x_{N2} \le 0,20$	$0 \le x_{N2} \le 0,55$
3	Carbon dioxide	$0 \le x_{CO2} \le 0,20$	$0 \le x_{CO2} \le 0,30$
4	Ethane	$0 \le x_{C2H6} \le 0,10$	$0 \le x_{C2H6} \le 0,25$
5	Propane	$0 \le x_{C3H8} \le 0,035$	$0 \le x_{C3H8} \le 0,14$
6 + 7	n-Butane + Isobutane[a]	$0 \le x_{C4H10} \le 0,015$	$0 \le x_{C4H10} \le 0,06$
8 + 9	n-Pentane + Isopentane[a]	$0 \le x_{C5H12} \le 0,005$	$0 \le x_{C5H12} \le 0,005$
10	n-Hexane	$0 \le x_{C6H14} \le 0,001$	$0 \le x_{C6H14} \le 0,002$
11	n-Heptane	$0 \le x_{C7H16} \le 0,000\,5$	$0 \le x_{C7H16} \le 0,001$
12 + 13 + 14	Octane+Nonane+Decane[a]	$0 \le x_{C8+} \le 0,000\,5$	$0 \le x_{C8+} \le 0,000\,5$
15	Hydrogen	$0 \le x_{H2} \le 0,10$	$0 \le x_{H2} \le 0,40$
16	Oxygen	$0 \le x_{O2} \le 0,000\,2$	$0 \le x_{O2} \le 0,02$
17	Carbon monoxide	$0 \le x_{CO} \le 0,03$	$0 \le x_{CO} \le 0,13$
18	Water	$0 \le x_{H2O} \le 0,000\,15$	$0 \le x_{H2O} \le 0,000\,2$
19	Hydrogen sulfide	$0 \le x_{H2S} \le 0,000\,2$	$0 \le x_{H2S} \le 0,27$
20	Helium	$0 \le x_{He} \le 0,005$	$0 \le x_{He} \le 0,005$
21	Argon	$0 \le x_{Ar} \le 0,000\,2$	$0 \le x_{Ar} \le 0,000\,5$

[a] Indicates the sum of the mole fractions of the components may not exceed the specified value.

NOTE 1 The method described in this part of the standard is applicable even for the individual pure components with high accuracy (i.e., to within experimental uncertainty). The tested ranges of application for temperature and pressure are given in Table 2.

NOTE 2 The accurate description of the thermodynamic properties of multi-component mixtures by the GERG-2008 equation of state is based on the accurate and wide-ranging equations for the binary subsystems, which were developed with experimental data that generally cover the entire composition range. Therefore, it can be expected that even multi-component natural gases of very unusual composition will be accurately described.

7 Uncertainty of the equation of state

7.1 Background

The uncertainties in this document are given at a 95 % confidence level (coverage factor k = 2). When ranges of uncertainties are given, the upper uncertainty value should be used unless further comparisons are made with the information given in references [1] and [2] to verify that the lower uncertainty value is valid for a particular application.

7.2 Uncertainty for pure gases

7.2.1 Natural gas main components

The estimated uncertainties in calculated density and speed of sound for the natural gas main components methane, nitrogen, carbon dioxide, and ethane are summarized in Table 7. For methane, more details are given in Figures 3 and 4; details for nitrogen, carbon dioxide, and ethane are given in [1],[2]. The estimated uncertainties in gas phase density and speed of sound range from 0,03 % to 0,05 % over wide ranges of temperature (e.g., up to 450 K, 350 °F) and at pressures up to 30 MPa (4 350 psia). In the liquid phase at pressures up to 30 MPa (4350 psia), the estimated uncertainties in density range from 0,05 % to 0,1 %. At higher temperatures or pressures, the estimated uncertainties in calculated speed of sound are generally higher than in calculated density because of less accurate data.

7.2.2 Secondary alkanes

The estimated uncertainties in calculated density, speed of sound, and isobaric heat capacity for the secondary alkanes propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane are summarized in Table 8. For calculated densities, an uncertainty of 0,2 % was estimated, whereas calculations of speed of sound and isobaric heat capacity have estimated uncertainties between 1 % and 2 %.

Table 7 — Uncertainties of the equations of state for the natural gas main components methane, nitrogen, carbon dioxide, and ethane with regard to different thermodynamic properties.

	Density	Speed of sound
Gas phase[a]		
$p \leq 30$ MPa (4350 psia)	0,03 % – 0,05 %	0,03 % – 0,05 %[b]
$p > 30$ MPa[c] (4350 psia)	0,1 % – 0,5 %	0,5 %[d]
Liquid phase		
$p \leq 30$ MPa (4350 psia)	0,05 % – 0,1 %	0,5 % – 1,5 %[e]
$p > 30$ MPa[c] (4350 psia)	0,5 %[f]	1,5 %[g]
Saturated liquid	0,05 %[h]	
Saturated vapour	0,05 %	

[a] for temperatures up to 450 K (350 °F); uncertainties at higher temperatures are given in Figures 3 and 4 for methane and in Reference [2] for nitrogen, carbon dioxide, and ethane.

[b] This uncertainty range is not valid over the entire temperature and pressure ranges specified in the table; further details are given in Figure 4 for methane and in Reference [2] for nitrogen, carbon dioxide, and ethane.

[c] States at pressures $p > 100$ MPa (14500 psia) are not included in the table due to their limited technical relevance, but can be obtained from Figures 3 and 4 for methane and from Reference [2] for nitrogen, carbon dioxide, and ethane.

[d] for methane; (1 – 2) % for nitrogen, (0,5 – 1) % for carbon dioxide, and ≥ 2 % for ethane; see Reference [2].

[e] for methane; 1 % ($p \leq 20$ MPa, 2900 psia) for nitrogen, (0,5 – 1) % for carbon dioxide, and (1 – 2) % for ethane; see Reference [2].

[f] for methane, nitrogen, and ethane; 1 % for carbon dioxide.

[g] for methane; ≥ 2 % ($p > 20$ MPa, 2900 psia) for nitrogen, (0,5 – 1) % for carbon dioxide, and ≥ 2 % for ethane; see Reference [2].

[h] for methane, nitrogen, and carbon dioxide; 0,1 % for ethane.

Table 8 — Uncertainties of the equations of state for propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, hydrogen sulfide, oxygen, and argon for various thermodynamic properties

Pressure range	Uncertainty in					
	$\rho(T,p)$	$w(T,p)$	$c_p(T,p)$	$p_s(T)$	$\rho'(T)$	$\rho''(T)$
$p \leq 30$ MPa (4350 psia)[a]	0,2 %[b]	(1 – 2) %[c]	(1 – 2) %[c]	0,2 %[d]	0,2 %	0,4 %[d,e]
$p > 30$ MPa (4350 psia)[f]	0,5 %	2 %	2 %	–	–	–

[a] Larger uncertainties exist in the extended critical region.

[b] In the extended critical region, $\Delta p/p$ is used instead of $\Delta\rho/\rho$.

[c] 1 % at gaseous and gas-like supercritical states, 2 % at liquid and liquid-like supercritical states.

[d] Larger relative uncertainties may result for small vapour pressures and their corresponding saturated vapour densities.

[e] Combination of the uncertainties of the gas densities and vapour pressures; experimental data with uncertainties of this level are available for only a few substances.

[f] States at pressures $p > 100$ MPa (14 500 psia) are not included due to their limited technical relevance.

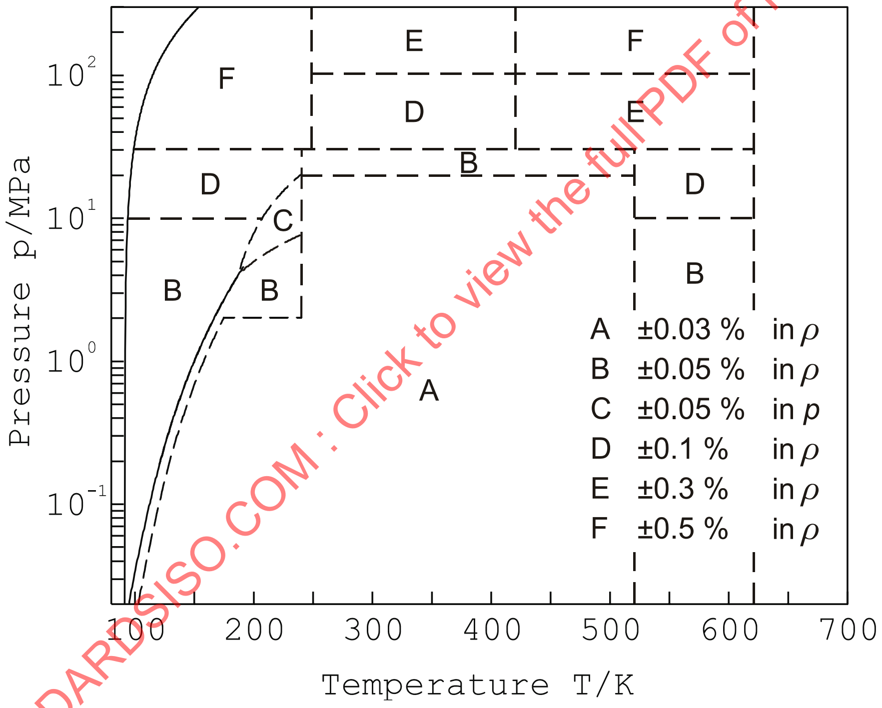

Figure 3 — Uncertainty diagram for densities of methane calculated from the GERG-2008 equation of state

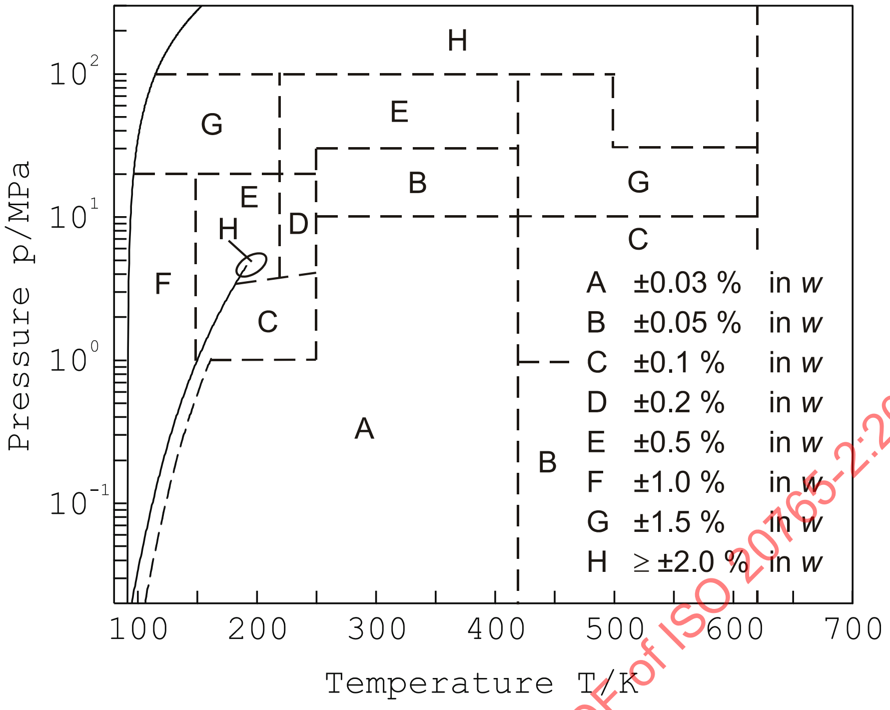

Figure 4 — Uncertainty diagram for speeds of sound of methane calculated from the GERG-2008 equation of state

7.2.3 Other secondary components

For oxygen and argon, the estimated uncertainties in calculated density, speed of sound, and isobaric heat capacity are as stated in Table 8 for the secondary alkanes.

The estimated uncertainties in calculated density for the other secondary components, namely hydrogen, carbon monoxide, hydrogen sulfide, and helium, at supercritical temperatures and for pressures up to 30 MPa (4350 psia) are less than 0,2 % and at higher pressures less than 0,5%. In general, higher uncertainties may occur in the liquid phase and for other thermodynamic properties.

For hydrogen at temperatures above 270 K (26 °F) and pressures up to 30 MPa (4350 psia), the uncertainty in calculated density is less than 0,1 %. At pressures above 30 MPa, the uncertainty in density is slightly higher, approximately (0,2 – 0,3) %. The equations for hydrogen and helium are designed to be valid at low (absolute) temperatures, which occur in their sub- and supercritical regions. This is of particular importance for the mixture model presented here since the reduced temperature range $1{,}2 \le T/T_c \le 1{,}8$ corresponds to the region where the highest accuracy in the description of thermodynamic properties of typical natural gases is demanded.

For water, calculated liquid densities and vapour pressures have an estimated uncertainty of 0,2 %. Other properties have higher uncertainties as detailed in [1],[2].

7.3 Uncertainty for binary mixtures

The most accurate binary mixture data were used for the development of the GERG-2008 equation of state. However, in regions where these data are not available, less accurate data were also taken into account for the development and assessment of the equation. Experimental data for multi-component mixtures were used for the validation of the quality of the equation only. The total uncertainties of the most accurate experimental binary and multi-component mixture data with respect to selected thermodynamic properties are listed in Table 9. The tabulated values represent the lowest uncertainties possible that can be achieved by the mixture model presented here. The corresponding experimental results are based on modern measurement techniques, which fulfil present quality standards. In contrast to the experimental uncertainties given for pure fluid properties measured using state-of-the-art techniques, the experimental uncertainties estimated for the properties of mixtures measured with the same apparatuses are, in general, higher due to the contribution of the uncertainty in the mixture composition.

Over wide ranges of temperature, pressure, and composition, the uncertainties tabulated below are mostly valid for those binary systems where binary specific departure functions were developed, see 6.2 and Table 4. Due to limited experimental data (e.g., accurate speed of sound measurements are available for only a few binary systems), the uncertainties are partly valid for the remaining binary mixtures, including those binary systems for which a generalized departure function was developed, see 6.2 and [1].

General estimates of the uncertainties of the GERG-2008 equation of state in the description of selected thermodynamic properties are given in Table 10. The different binary mixtures are distinguished by adjusted reducing functions with a binary specific departure function, adjusted reducing functions with a generalized departure function, or only adjusted reducing functions (without a departure function). Uncertainty values are given for different pressures, temperatures, and (approximate) reduced temperature ranges.

Table 9 — Relative experimental uncertainties of the most accurate binary and multi-component mixture data

Data type	Property	Relative uncertainty
Density (gas phase)	$\Delta\rho/\rho$	≤ (0,05 – 0,1) %
Density (liquid phase)	$\Delta\rho/\rho$	≤ (0,1 – 0,3) %
Isochoric heat capacity	$\Delta c_v/c_v$	≤ (1 – 2) %
Speed of sound (gas phase)	$\Delta w/w$	≤ (0,05 – 0,1) %
Isobaric heat capacity	$\Delta c_p/c_p$	≤ (1 – 2) %
Enthalpy differences (gas phase)	$\Delta(\Delta h)/\Delta h$	≤ (0,2 – 0,5) %
Saturated liquid density	$\Delta\rho'/\rho'$	≤ (0,1 – 0,2) %
VLE data	$\Delta p_s/p_s$	≤ (1 – 3) %
NOTE Δh indicates a difference between two state points, $h(T_2,p_2) - h(T_1,p_1)$.		

Table 10 — Uncertainty of the GERG-2008 equation of state in the description of selected volumetric and caloric properties of different binary mixtures[a]

Mixture region[b]	Adjusted reducing functions with a		Only adjusted reducing functions (no departure function)
	binary specific departure function	generalized departure function	
Gas phase 0 – 30 MPa (4 350 psia) $1{,}2 \le T/T_r \le 1{,}4$	$\Delta\rho/\rho \le 0{,}1$ %	$\Delta\rho/\rho \le (0{,}1 - 0{,}2)$ %	$\Delta\rho/\rho \le (0{,}5 - 1)$ %
Gas phase 0 – 30 MPa (4 350 psia) $1{,}4 \le T/T_r \le 2{,}2$	$\Delta\rho/\rho \le 0{,}1$ %	$\Delta\rho/\rho \le 0{,}1$ %	$\Delta\rho/\rho \le (0{,}3 - 0{,}5)$ %
Gas phase 0 – 20 MPa (2 900 psia) $1{,}2 \le T/T_r \le 1{,}4$	$\Delta w/w \le 0{,}1$ %	$\Delta w/w \le 0{,}5$ %	$\Delta w/w \le 1$ %
Gas phase 0 – 20 MPa (2 900 psia) $1{,}4 \le T/T_r \le 2{,}2$	$\Delta w/w \le 0{,}1$ %	$\Delta w/w \le 0{,}3$ %	$\Delta w/w \le 0{,}5$ %
Saturated liquid state 100 K ≤ T ≤ 140 K (–280 °F ≤ T ≤ –208 °F)	$\Delta\rho'/\rho' \le (0{,}1 - 0{,}2)$ %	$\Delta\rho'/\rho' \le (0{,}2 - 0{,}5)$ %	$\Delta\rho'/\rho' \le (0{,}5 - 1)$ %
Liquid phase 0 – 40 MPa (5 800 psia) $T/T_r \le 0{,}7$	$\Delta\rho/\rho \le (0{,}1 - 0{,}3)$ %	$\Delta\rho/\rho \le (0{,}2 - 0{,}5)$ %	$\Delta\rho/\rho \le (0{,}5 - 1)$ %

Table 10 *(continued)*

Mixture region[b]	Adjusted reducing functions with a binary specific departure function	Adjusted reducing functions with a generalized departure function	Only adjusted reducing functions (no departure function)

[a] The relative uncertainty in isobaric and isochoric heat capacity is estimated to be less than (1 – 2) % in the homogeneous gas, liquid, and supercritical regions independent of the type of binary equation.

[b] For a typical lean natural gas or liquid natural gas, temperatures of 140 K (–208 °F), 250 K (–10 °F), 300 K (80 °F), and 350 K (170 °F) correspond to reduced temperatures $T/T_r(\bar{x}) = 1/\tau$ of about: 0,7; 1,3; 1,5; and 1,8.

From Table 10 it is evident that binary systems with a binary specific departure function generally have the lowest uncertainty for the different properties as compared to the other binary systems with either a generalized departure function or only modified reducing parameters. Gas phase densities and speeds of sound have uncertainties of ≤ 0,1 % for binary mixtures with a binary specific departure function. The relative uncertainty in isobaric and isochoric heat capacity is estimated to be less than (1 – 2) % in the homogeneous gas, liquid, and supercritical regions independent of the type of developed binary equation.

7.4 Uncertainty for natural gases

The GERG-2008 wide-range equation of state for natural gases and other (multi-component and binary) mixtures, consisting of the components listed in Table 6, is valid in the gas phase, in the liquid phase, in the supercritical region, and for vapour-liquid equilibrium states. For natural gases and similar mixtures, normal and full ranges were defined. The extrapolation to temperatures and pressures yields reasonable results even far beyond the full range of application. The estimated uncertainties for the different ranges of application, as described below, are based on the representation of the available experimental data for various thermodynamic properties of natural gases and other multi-component mixtures by the GERG-2008 equation of state as summarized in Table 11.

In general, there are no restrictions in the composition range of binary and multi-component mixtures. But, since the estimated uncertainty of the GERG-2008 equation of state is based on the experimental data used for the development and evaluation of the equation, the uncertainty is mostly unknown for composition ranges not covered by experimental data. The data situation allows for well-founded uncertainty estimates only for selected properties and parts of the fluid $p\rho T$ surface.

Most of the available experimental data for multi-component mixtures describe the $p\rho T$ relation of natural gases and similar mixtures in the gas phase. The majority of these data cover the temperature range 270 K ≤ T ≤ 350 K at pressures up to 30 MPa[1],[2] and were measured for pipeline quality natural gas. There are a number of additional experimental data available that define the composition range of intermediate quality natural gas, e.g., measurements on rich natural gases with comparatively high content of carbon dioxide, ethane, propane, and n-butane; see Table 6 for the composition ranges defined for pipeline quality and intermediate quality natural gases. As mentioned in 6.3, pipeline quality natural gases are a subset of the intermediate quality natural gases.

Table 11 — Summary of the available data for volumetric and caloric properties of natural gases and other multi-component mixtures

Data type[a]	Number of data points	Covered ranges Temperature T/K	 Pressure p/MPa	Maximum number of components
Density	21769	91,0 – 573	0,03 – 99,9	18
Speed of sound	1337	213 – 414	0,00 – 70,0	13
Isobaric heat capacity	325	105 – 350	0,5 – 30,0	8
Enthalpy differences	1166	105 – 422	0,2 – 16,5	10

[a] Further data not included in Table 11 were used to validate the quality of the GERG-2008 equation of state, e.g., recent dew-point measurements for a number of different natural gases and other multi-component mixtures, see [1], [2].

Table 11 *(continued)*

Data type[a]	Number of data points	Covered ranges		Maximum number of components
		Temperature	Pressure	
		T/K	p/MPa	
Saturated liquid density	124	105 – 251	0,04 – 3,2	8
VLE data	2284	77,8 – 450	0,1 – 27,6	4
Total	27005	77,8 – 573	0,00 – 99,9	18

[a] Further data not included in Table 11 were used to validate the quality of the GERG-2008 equation of state, e.g., recent dew-point measurements for a number of different natural gases and other multi-component mixtures, see [1], [2].

7.4.1 Uncertainty in the normal and intermediate ranges of applicability of natural gas

The normal range of applicability of natural gas covers the temperature range 90 K ≤ T ≤ 450 K for pressures up to 35 MPa, see 6.3, Table 5. This range corresponds to the use of the equation in both standard and advanced technical applications using natural gases and similar mixtures, e.g., pipeline transport, natural gas storage, and improved processes with liquefied natural gas. Estimated uncertainties for the composition subsets “pipeline quality natural gas” and “intermediate quality natural gas” are summarized in Table 12.

Table 12 — Uncertainty of the GERG-2008 equation of state in the description of selected volumetric and caloric properties

Pipeline quality natural gas	Temperature region	Pressure region	Uncertainty
Density, gas phase	$250 \le T/\mathrm{K} \le 450$	$p/\mathrm{MPa} \le 35$	$\Delta\rho/\rho \le 0{,}1$ %
Density, liquid phase	$100 \le T/\mathrm{K} \le 140$	$p/\mathrm{MPa} \le 40$	$\Delta\rho/\rho \le (0{,}1 - 0{,}5)$ %
Saturated liquid density	$100 \le T/\mathrm{K} \le 140$		$\Delta\rho'/\rho' \le (0{,}1 - 0{,}3)$ %
Speed of sound, gas phase	$250 \le T/\mathrm{K} \le 270$	$p/\mathrm{MPa} \le 12$	$\Delta w/w \le 0{,}1$ %
	$270 \le T/\mathrm{K} \le 450$	$p/\mathrm{MPa} \le 20$	$\Delta w/w \le 0{,}1$ %
	$250 \le T/\mathrm{K} \le 270$	$12 \le p/\mathrm{MPa} \le 20$	$\Delta w/w \le (0{,}2 - 0{,}3)$ %
	$250 \le T/\mathrm{K} \le 450$	$20 \le p/\mathrm{MPa} \le 30$	$\Delta w/w \le (0{,}2 - 0{,}3)$ %
Enthalpy differences (gas)	$250 \le T/\mathrm{K} \le 350$	$p/\mathrm{MPa} \le 20$	$\Delta(\Delta h)/\Delta h \le (0{,}2 - 0{,}5)$ %
Enthalpy differences, liquid phase			$\Delta(\Delta h)/\Delta h \le (0{,}5 - 1{,}0)$ %
Isobaric and isochoric heat capacities, gas and liquid phases			$\Delta c_p/c_p$ or $\Delta c_v/c_v \approx (1 - 2)$ %
Intermediate range[a]	Molar mass	Pressure region	Uncertainty
Density, gas phase	$M \le 26\ \mathrm{kg{\cdot}kmol^{-1}}$	$p/\mathrm{MPa} \le 30$	$\Delta\rho/\rho \le 0{,}1$ %
	$M > 26\ \mathrm{kg{\cdot}kmol^{-1}}$	$p/\mathrm{MPa} \le 30$	$\Delta\rho/\rho \le (0{,}1 - 0{,}3)$ %[b]

[a] For rich natural gases, i.e., for natural gas mixtures that contain comparatively large amounts of carbon dioxide, ethane, propane, and further secondary alkanes, the tested temperature range is 280 K ≤ T ≤ 350 K (44 °F ≤ T ≤ 70 °F).

[b] For mixtures with molar masses $M > 30\ \mathrm{kg{\cdot}kmol^{-1}}$ and compositions within the limits stated in Table 6, the upper uncertainty value in density is estimated to be 0,5 %.

7.4.1.1 Pipeline quality natural gas

Density data in the gas phase for pipeline quality natural gases are described by the equation with an uncertainty of $\Delta\rho/\rho \le 0{,}1$ % over the temperature range 250 K ≤ T ≤ 450 K (–10 °F ≤ T ≤ 350 °F) and for pressures up to 35 MPa (5075 psia). The uncertainty in speed of sound is likewise less than 0,1%. However, due to limited experimental data, this uncertainty is restricted to pressures below 20 MPa (2900 psia), and at temperatures below 270 K (26 °F) it is restricted to pressures below 12 MPa

(1740 psia). The most accurate liquid or saturated liquid density data are described to within 0,1 % to 0,3 %, which is in agreement with the estimated experimental uncertainty of the measurements.

7.4.1.2 Intermediate quality natural gas

This quality range of natural gases expands the composition range of the pipeline quality natural gases. The intermediate composition range is almost identical to the composition range covered by the available experimental natural gas and similar multi-component mixture data, including several data sets for natural gases containing synthetic mixtures, ternary mixtures of natural gas main components, and rich natural gases. Rich natural gases contain large amounts of carbon dioxide (up to 0,20 mole fraction), ethane (up to 0,18), propane (up to 0,14), n-butane (up to 0,06), n-pentane (0,005), and n-hexane (0,002).

For mixtures that fall within the intermediate composition range defined in Table 6, the estimated uncertainty in gas phase density is ≤ 0,1 % for molar masses $M \leq 26$ kg·kmol^{-1}; see equation (18) for the calculation of the molar mass from the given mixture composition. For mixtures with molar masses $M > 26$ kg·kmol^{-1}, the uncertainty in gas phase density is 0,1 % to 0,3 %. For other thermodynamic properties, well-founded estimates of uncertainty cannot be given due to the limited data situation.

NOTE 1 For rich natural gases, the lower temperature limit is increased because dew point temperatures are considerably higher for these types of mixtures, which contain comparatively large amounts of carbon dioxide, ethane, propane, and the further secondary alkanes.

NOTE 2 Within the mole fraction limits defined for pipeline quality natural gas, the molar mass of any mixture will always be lower than 26 kg·kmol^{-1}.

7.4.2 Uncertainty in the full range of applicability, and calculation of properties beyond this range

The full range of application covers temperatures of 60 K ≤ T ≤ 700 K (−352 °F ≤ T ≤ 800 °F) and pressures up to 70 MPa (10150 psia). The uncertainty of the equation in gas phase density at temperatures and pressures within this range is roughly (0,2 – 0,5) %, except for states near the critical region. For certain mixtures, the full range of application covers temperatures of $T > 700$ K (800 °F) and pressures of $p > 70$ MPa (10150 psia). For example, the equation accurately describes gas phase density data of air to within ±(0,1 – 0,2) % at temperatures up to 900 K and pressures up to 90 MPa. For other thermodynamic properties, well-founded estimates of uncertainty cannot be given due to the limited data situation outside the normal range of application.

When larger uncertainties are acceptable, tests have shown that the equation can be reasonably used outside the full range of application. For example, density data (frequently of questionable and low accuracy) for certain binary mixtures are described to within ±(0,5 – 1) % at pressures up to 100 MPa and more.

7.5 Uncertainties in other properties

For pipeline quality natural gas, similar types of properties will have similar uncertainties to those listed in Table 12. For example, energies and entropies will have uncertainties similar to those in enthalpy, and uncertainties in Joule-Thomson values will be similar to those in heat capacities.

7.6 Impact of uncertainties of input variables

The user should recognize that uncertainties in the input variables, usually pressure, temperature and composition in mole fractions, will have additional effects upon the uncertainty of any calculated result. The uncertainties given so far for calculated results assume that the input data are exact. In any particular application where the additional uncertainty may be of importance, the user should carry out sensitivity tests to determine its magnitude.

8 Reporting of results

Results for the thermodynamic properties shall be given with the number of significant figures that are appropriate for the uncertainties listed in Tables 7 through 10. The report shall identify the temperature, pressure (or density), and detailed composition to which the results refer. The method of calculation used shall be identified by reference to ISO 20765-2 Natural gas – Calculation of Thermodynamic Properties.

For example, for pure methane at 25 °C, 0,101 325 MPa, Z is calculated as 0,998 2511. Taking the expanded uncertainty from Table 7 to be that of the gas phase density, 0,03%, this is 0,000 299 48. This is rounded to two significant figures, 0,000 30, and Z is reported in accordance with this uncertainty, i.e., 0,998 25. Thus, one would report Z(methane, 298,15 K, 0,101 325 MPa) = 0,998 25 ±0,000 30 (95 % confidence).

As a second example, for pure liquid methane at its normal boiling point (111,66 K, 0,101 325 MPa), Z is calculated as 0,004 145 252. Taking the expanded uncertainty from Table 7 to be that of the liquid phase density, 0,05 %, this is 0,000 002 0726. This is rounded to two significant figures, 0,000 0021, and Z is reported in accordance with this uncertainty, i.e., 0,004 1453. Thus, one would report Z (methane, 111,66 K, 0,101 325 MPa) = 0,004 1453 ±0,000 0021 (95 % confidence).

For the validation of calculations and for subsequent calculations based on thermodynamic properties obtained using this standard, it may be appropriate to carry extra digits (see example calculations in Annex G).

Annex A
(normative)

Symbols and units

Symbol	Meaning	First Use of Symbol	Units
a	Molar Helmholtz free energy	equation (1)	kJ/kmol
B	Second virial coefficient	equation (32)	m^3/kmol
c	Density exponent	equation (9)	---
c_p	Molar isobaric heat capacity	equation (26)	kJ/(kmol·K)
c_v	Molar isochoric heat capacity	equation (24)	kJ/(kmol·K)
C	Third virial coefficient	equation (33)	m^6/kmol^2
C_v	Specific isochoric heat capacity	Table 1	kJ/(kg·K)
C_p	Specific isobaric heat capacity	Table 1	kJ/(kg·K)
d	Density exponent	equation (9)	---
D	Mass-based density	equation (19)	kg/m^3
F	Mixture parameter	equation (11)	---
g	Molar Gibbs free energy	equation (27)	kJ/kmol
h	Molar enthalpy	equation (25)	kJ/kmol
H	Specific enthalpy	Table 1	kJ/kg
i	Serial number	equation (6)	---
j	Serial number	equation (10)	---
k	Coverage factor	Scope	---
k	Serial number	equation (7)	---
K	Number of terms	equation (9)	---
m	Molar mass	equation (18)	kg/kmol
n	Coefficient	equation (7)	---
N	Number of components in the mixture	equation (6)	---
p	Pressure	equation (20)	MPa
R	Molar gas constant, R = 8,314 472,[4]	equation (7)	kJ/(kmol·K)
R^*	Molar gas constant, R^*= 8,314 51, used in [5]	equation (7)	kJ/(kmol·K)
s	Molar entropy	equation (23)	kJ/(kmol·K)
S	Specific entropy	Table 1	kJ/(kg·K)
t	Temperature exponent	equation (9)	---
T	Temperature in K (ITS-90)	equation (1)	K
u	Molar internal energy	equation (22)	kJ/kmol
U	Specific internal energy	Table 1	kJ/kg
v	Molar volume	equation (20)	M^3/kmol
w	Speed of sound	equation (28)	m/s
x	Mole fraction	equation (6)	---
$\overline{x}$	Molar composition (vector of mole fractions)	equation (1)	---

Symbol	Meaning	First Use of Symbol	Units
z	Any property	equation (37)	
Z	Compression factor	equation (21)	---
Greek Symbols			
α	Reduced molar Helmhotz free energy, $\alpha = a/(RT)$	equation (2)	---
β	Parameter	equation (12)	---
β_T	Parameter	equation (14)	---
β_V	Parameter	equation (13)	---
γ	Parameter	equation (12)	---
γ_T	Parameter	equation (14)	---
γ_V	Parameter	equation (13)	---
δ	Reduced density, $\delta = \rho/\rho_r$	equation (2)	---
ϕ	Isothermal throttling coefficient	equation (30)	m^3/kmol
ε	Parameter	equation (12)	---
∂	Partial derivative	equation (15)	---
$\Delta\alpha$	Departure function for the reduced molar Helmholtz free energy	equation (5)	---
η	Parameter	equation (12)	---
ϑ	Parameter	equation (7)	---
κ	Isentropic exponent	equation (31)	---
μ	Joule-Thomson coefficient	equation (29)	K/MPa
ρ	Molar density	equation (1)	kmol/m^3
τ	Inverse reduced temperature, $\tau = T_r/T$	equation (2)	---
Inferior indices			
c	At the critical point	equation (7)	---
Exp	Exponential term	equation (9)	---
i	Serial number	equation (6)	---
j	Serial number	equation (10)	---
k	Serial number	equation (7)	---
o	Property of the pure substance	equation (5)	---
Pol	Polynomial term	equation (9)	---
r	Reducing property	equation (3)	---
s	At saturation (phase equilibrium)	Table 8	---
δ	Partial derivative with respect to δ	equation (15)	---
τ	Partial derivative with respect to τ	equation (15)	---
0	Reference state, T_0 = 298,15 K, p_0 = 0,101325 MPa	equation (B.4)	---
Superior indices			
o	Ideal-gas state	equation (1)	---
r	Residual part	equation (1)	---
ʻ	Saturated liquid state	Table 8	---
“	Saturated vapour state	Table 8	---

Annex B
(normative)

The reduced Helmholtz free energy of the ideal gas

B.1 Calculation of the reduced Helmholtz free energy of the ideal gas

For a pure component, the Helmholtz free energy of the ideal gas is given by

$$a^{\mathrm{o}}(\rho,T)=h^{\mathrm{o}}(T)-RT-Ts^{\mathrm{o}}(\rho,T) \tag{B.1}$$

For the ideal gas, the enthalpy h^{o} is a function of temperature only, whereas the entropy s^{o} depends on temperature and density. Both properties can be expressed in terms of the ideal-gas isobaric heat capacity c_p^{o} as follows:

$$h^{\mathrm{o}}(T)=\int_{T_0}^{T} c_p^{\mathrm{o}}\,\mathrm{d}T+h_0^{\mathrm{o}} \tag{B.2}$$

$$s^{\mathrm{o}}(\rho,T)=\int_{T_0}^{T}\frac{c_p^{\mathrm{o}}-R}{T}\,\mathrm{d}T-R\ln\left(\frac{\rho}{\rho_0^{\mathrm{o}}}\right)+s_0^{\mathrm{o}} \tag{B.3}$$

When the above expressions for $h^{\mathrm{o}}(T)$ and $s^{\mathrm{o}}(\rho,T)$ are inserted into equation (B.1), one obtains

$$a^{\mathrm{o}}(\rho,T)=\left[\int_{T_0}^{T} c_p^{\mathrm{o}}\,\mathrm{d}T+h_0^{\mathrm{o}}\right]-RT-T\left[\int_{T_0}^{T}\frac{c_p^{\mathrm{o}}-R}{T}\,\mathrm{d}T-R\ln\left(\frac{\rho}{\rho_0^{\mathrm{o}}}\right)+s_0^{\mathrm{o}}\right] \tag{B.4}$$

where

all variables with the subscript "0" refer to an arbitrary reference state. The reference state of zero enthalpy and zero entropy is here adopted at T_0 = 298,15 K and p_0 = 0,101 325 MPa for the ideal gas. The integration constants h_0^{o} and s_0^{o} are then determined so as to conform to this definition. The reference density ρ_0^{o} is given by $\rho_0^{\mathrm{o}} = p_0/(RT_0)$.

In order to obtain an explicit equation for $a^{\mathrm{o}}(\rho,T)$, an equation for the ideal-gas isobaric heat capacity c_p^{o} is needed. The ideal-gas isobaric heat capacity may be written as follows [1], [2],

$$\frac{c_p^{\mathrm{o}}}{R}=1+n_3^{\mathrm{o}}+\sum_{k=4,6} n_k^{\mathrm{o}}\left(\frac{\vartheta_k^{\mathrm{o}}\dfrac{T_{\mathrm{c}}}{T}}{\sinh\left(\vartheta_k^{\mathrm{o}}\dfrac{T_{\mathrm{c}}}{T}\right)}\right)^2+\sum_{k=5,7} n_k^{\mathrm{o}}\left(\frac{\vartheta_k^{\mathrm{o}}\dfrac{T_{\mathrm{c}}}{T}}{\cosh\left(\vartheta_k^{\mathrm{o}}\dfrac{T_{\mathrm{c}}}{T}\right)}\right)^2 \tag{B.5}$$

The values of the coefficients n_k^{o} and parameters ϑ_k^{o} of equation (B.5) are given in Table B.1.

NOTE 1 The equation for the ideal-gas isobaric heat capacity is taken from [5] and given as a function of the temperature T. The values resulting from the parameter product $\vartheta_k^{\mathrm{o}}\ T_{\mathrm{c}}$ (for k = 4 to 7) are in agreement with the original parameters D^{o}, F^{o}, H^{o}, and J^{o}, respectively, and the coefficients n_k^{o} (for k = 4 to 7) have identical values as the coefficients C^{o}, E^{o}, G^{o}, and I^{o}, respectively. The coefficient $n_3^{\mathrm{o}} = B^{\mathrm{o}}-1$.

For a mixture at a given mixture density ρ, temperature T, and molar composition $\bar{x}$, the reduced Helmholtz free energy of the ideal gas is given as follows:

$$\alpha^{\mathrm{o}}(\rho,T,\bar{x})=\sum_{i=1}^{N}x_i\left[\alpha_{\mathrm{oi}}^{\mathrm{o}}(\rho,T)+\ln x_i\right] \tag{B.6}$$

In this equation, $\alpha_{\mathrm{oi}}^{\mathrm{o}}(\rho,T)$ is the dimensionless form of the Helmholtz free energy in the ideal-gas state of component i as given by

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

where

the term $\sum x_i \ln x_i$ accounts for the entropy of mixing of the ideal-gas mixture.

NOTE 2 To indicate a pure substance as a component in a mixture, the inferior indices “o” (referring to pure substance) and “*i*” (referring to the considered component) are introduced.

It is important to observe that in equation (B.6) α^{o} is a function of the molar density ρ, the temperature T, and the molar composition $\bar{x}$, where ρ is the molar density of the real mixture (i.e., not the molar density of the ideal gas). If the input variables are the absolute pressure p, the temperature T and the molar composition $\bar{x}$, ρ may be calculated from the input variables as described in 5.

B.2 Derivatives of the reduced Helmholtz free energy of the ideal gas

$$\alpha_{\delta}^{\mathrm{o}}=\left(\frac{\partial\alpha^{\mathrm{o}}}{\partial\delta}\right)_{\tau,\bar{x}}=\sum_{i=1}^{N}x_i\frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}}\left(\frac{\partial\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)}\right)_T=\frac{\rho_{\mathrm{r}}}{\rho} \tag{B.8}$$

$$\alpha_{\delta\delta}^{\mathrm{o}}=\left(\frac{\partial^2\alpha^{\mathrm{o}}}{\partial\delta^2}\right)_{\tau,\bar{x}}=\sum_{i=1}^{N}x_i\left(\frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}}\right)^2\left(\frac{\partial^2\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)^2}\right)_T=-\frac{\rho_{\mathrm{r}}^2}{\rho^2} \tag{B.9}$$

$$\alpha_{\delta\tau}^{\mathrm{o}}=\left(\frac{\partial^2\alpha^{\mathrm{o}}}{\partial\delta\partial\tau}\right)_{\bar{x}}=\sum_{i=1}^{N}x_i\frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}}\frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}}\left(\frac{\partial^2\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)\partial\left(T_{\mathrm{c},i}/T\right)}\right)=0 \tag{B.10}$$

$$\alpha_{\tau}^{\mathrm{o}}=\left(\frac{\partial\alpha^{\mathrm{o}}}{\partial\tau}\right)_{\delta,\bar{x}}=\sum_{i=1}^{N}x_i\frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}}\left(\frac{\partial\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(T_{\mathrm{c},i}/T\right)}\right)_{\rho} \tag{B.11}$$

$$\left(\frac{\partial\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(T_{\mathrm{c},i}/T\right)}\right)_{\rho}=\frac{R^*}{R}\left[n_{\mathrm{oi},2}^{\mathrm{o}}+n_{\mathrm{oi},3}^{\mathrm{o}}\frac{T}{T_{\mathrm{c},i}}+\sum_{k=4,6}n_{\mathrm{oi},k}^{\mathrm{o}}\frac{\vartheta_{\mathrm{oi},k}^{\mathrm{o}}}{\tanh\left(\vartheta_{\mathrm{oi},k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)}-\sum_{k=5,7}n_{\mathrm{oi},k}^{\mathrm{o}}\vartheta_{\mathrm{oi},k}^{\mathrm{o}}\tanh\left(\vartheta_{\mathrm{oi},k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right] \tag{B.12}$$

$$\alpha_{\tau\tau}^{\mathrm{o}}=\left(\frac{\partial^2\alpha^{\mathrm{o}}}{\partial\tau^2}\right)_{\delta,\bar{x}}=\sum_{i=1}^{N}x_i\left(\frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}}\right)^2\left(\frac{\partial^2\alpha_{\mathrm{oi}}^{\mathrm{o}}}{\partial\left(T_{\mathrm{c},i}/T\right)^2}\right)_{\rho} \tag{B.13}$$

$$\left(\frac{\partial^2\alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(T_{\mathrm{c},i}/T\right)^2}\right)_\rho = \frac{R^*}{R}\left[-n^{\mathrm{o}}_{\mathrm{o}i,3}\left(\frac{T}{T_{\mathrm{c},i}}\right)^2 - \sum_{k=4,6} n^{\mathrm{o}}_{\mathrm{o}i,k}\frac{\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\right)^2}{\left(\sinh\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\dfrac{T_{\mathrm{c},i}}{T}\right)\right)^2} - \sum_{k=5,7} n^{\mathrm{o}}_{\mathrm{o}i,k}\frac{\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\right)^2}{\left(\cosh\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\dfrac{T_{\mathrm{c},i}}{T}\right)\right)^2}\right]$$

(B.14)

Table B.1 — Values of the coefficients and parameters in equation (B.7) for the 21 componentsa

k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$	k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$
		Methane			
1	19,597 508 817	–	5	0,004 60	0,936 220 902
2	–83,959 667 892	–	6	8,744 32	5,577 233 895
3	3,000 88	–	7	–4,469 21	5,722 644 361
4	0,763 15	4,306 474 465			
		Nitrogen			
1	11,083 407 489	–	5	–0,146 60	5,393 067 706
2	–22,202 102 428	–	6	0,900 66	13,788 988 208
3	2,500 31	–	7	–	–
4	0,137 32	5,251 822 620			
		Carbon dioxide			
1	11,925 152 758	–	5	–1,060 44	2,844 425 476
2	–16,118 762 264	–	6	2,033 66	1,589 964 364
3	2,500 02	–	7	0,013 93	1,121 596 090
4	2,044 52	3,022 758 166			
		Ethane			
1	24,675 437 527	–	5	1,237 22	0,731 306 621
2	–77,425 313 760	–	6	13,197 4	3,378 007 481
3	3,002 63	–	7	–6,019 89	3,508 721 939
4	4,339 39	1,831 882 406			
		Propane			
1	31,602 908 195	–	5	3,197 00	0,543 210 978
2	–84,463 284 382	–	6	19,192 1	2,583 146 083
3	3,029 39	–	7	–8,372 67	2,777 773 271
4	6,605 69	1,297 521 801			
		n-Butane			
1	20,884 143 364	–	5	6,894 06	0,431 957 660
2	–91,638 478 026	–	6	24,461 8	4,502 440 459

Table B.1 *(continued)*

k	$n^{o}_{oi,k}$	$\vartheta^{o}_{oi,k}$	k	$n^{o}_{oi,k}$	$\vartheta^{o}_{oi,k}$
3	3,339 44	–	7	14,782 4	2,124 516 319
4	9,448 93	1,101 487 798			
Isobutane					
1	20,413 726 078	–	5	5,251 56	0,485 556 021
2	−94,467 620 036	–	6	25,142 3	4,671 261 865
3	3,067 14	–	7	16,138 8	2,191 583 480
4	8,975 75	1,074 673 199			
n-Pentane					
1	28,587 336 516	–	5	21,836 0	1,789 520 971
2	−96,265 336 649	–	6	33,403 2	3,777 411 113
3	3,0	–	7	–	–
4	8,950 43	0,380 391 739			
Isopentane					
1	29,158 561 921	–	5	20,110 1	1,977 271 641
2	−111,216 048 893	–	6	33,168 8	4,169 371 131
3	3	–	7	–	–
4	11,761 8	0,635 392 636			
n-Hexane					
1	32,499 459 095	–	5	26,814 2	1,691 951 873
2	−103,869 150 117	–	6	38,616 4	3,596 924 107
3	3,0	–	7	–	–
4	11,697 7	0,359 036 667			
n-Heptane					
1	37,237 679 271	–	5	30,470 7	1,548 136 560
2	−105,724 194 520	–	6	43,556 1	3,259 326 458
3	3,0	–	7	–	–
4	13,726 6	0,314 348 398			
n-Octane					
1	42,143 183 464	–	5	33,8029	1,431 644 769
2	−106,349 263 157	–	6	48,1731	2,973 845 992
3	3,0	–	7	–	–
4	15,686 5	0,279143540			
n-Nonane					
1	46,723 625 203	–	5	38,123 50	1,370 586 158
2	−112,017 705 837	–	6	53,341 50	2,848 860 483

Table B.1 *(continued)*

k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$	k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$
3	3,0	–	7	–	–
4	18,024 10	0,263 819 696			
n-Decane					
1	50,353 023 354	–	5	43,493 10	1,353 835 195
2	–120,012 066 480	–	6	58,365 70	2,833 479 035
3	3,0	–	7	–	–
4	21,006 90	0,267 034 159			
Hydrogen					
1	13,796 443 393	–	5	0,454 44	9,847 634 830
2	–175,864 487 294	–	6	1,560 39	49,765 290 750
3	1,479 06	–	7	–1,375 60	50,367 279 301
4	0,958 06	6,891 654 113			
Oxygen					
1	10,001 843 586	–	5	1,013 34	7,223 325 463
2	–14,996 095 135	–	6	–	–
3	2,501 46	–	7	–	–
4	1,075 58	14,461 722 565			
Carbon monoxide					
1	10,813 340 744	–	5	0,004 93	5,302 762 306
2	–19,834 733 959	–	6	–	–
3	2,500 55	–	7	–	–
4	1,028 65	11,669 802 800			
Water					
1	8,216 535 516	–	5	0,987 63	1,763 895 929
2	–12,002 441 239	–	6	3,069 04	3,874 803 739
3	3,003 92	–	7	–	–
4	0,010 59	0,415 386 589			
Hydrogen sulfide					
1	9,336 197 742	–	5	1,002 43	2,270 653 980
2	–16,266 508 995	–	6	–	–
3	3,0	–	7	–	–
4	3,119 42	4,914 580 541			
Helium					
1	13,628 409 737	–	3	1,5	–
2	–143,470 759 602	–			

Table B.1 *(continued)*

k	$n^{\mathrm{o}}_{\mathrm{oi},k}$	$\vartheta^{\mathrm{o}}_{\mathrm{oi},k}$	k	$n^{\mathrm{o}}_{\mathrm{oi},k}$	$\vartheta^{\mathrm{o}}_{\mathrm{oi},k}$
Argon					
1	8,316 631 500	–	3	1,5	–
2	−4,946 502 600	–			

[a] The values of the coefficients and parameters are also valid for equation (7).

Annex C
(normative)

Values of critical parameters and molar masses of the pure components

Table C.1 — Critical parameters and molar masses of the 21 components

Component	Formula	$\rho_{c,i}$/(mol·dm^{-3})	$T_{c,i}$/K	M_i/(g·mol^{-1})[a]
Methane	CH_4	10,139 342 719	190,564	16,042 46
Nitrogen	N_2	11,183 9	126,192	28,013 4
Carbon dioxide	CO_2	10,624 978 698	304,1282	44,009 5
Ethane	C_2H_6	6,870 854 540	305,322	30,069 04
Propane	C_3H_8	5,000 043 088	369,825	44,095 62
n-Butane	C_4H_{10}	3,920 016 792	425,125	58,122 2
Isobutane	C_4H_{10}	3,860 142 940	407,817	58,122 2
n-Pentane	C_5H_{12}	3,215 577 588	469,7	72,148 78
Isopentane	C_5H_{12}	3,271	460,35	72,148 78
n-Hexane	C_6H_{14}	2,705 877 875	507,82	86,175 36
n-Heptane	C_7H_{16}	2,315 324 434	540,13	100,201 94
n-Octane	C_8H_{18}	2,056 404 127	569,32	114,228 52
n-Nonane	C_9H_{20}	1,81	594,55	128,255 1
n-Decane	$C_{10}H_{22}$	1,64	617,7	142,281 68
Hydrogen	H_2	14,94	33,19	2,015 88
Oxygen	O_2	13,63	154,595	31,998 8
Carbon monoxide	CO	10,85	132,86	28,010 1
Water	H_2O	17,873 716 090	647,096	18,015 28
Hydrogen sulfide	H_2S	10,19	373,1	34,080 88
Helium	He	17,399	5,1953	4,002 602
Argon	Ar	13,407 429 659	150,687	39,948

[a] According to IUPAC Technical Report (2006),[6] calculated using the exact atomic masses in the IUPAC report.

Annex D
(normative)

The residual part of the reduced Helmholtz free energy

D.1 Calculation of the residual part of the reduced Helmholtz free energy

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

$$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})=\alpha_{\mathrm{o}}^{\mathrm{r}}(\delta,\tau,\bar{x})+\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{D.1}$$

where

$$\alpha_{\mathrm{o}}^{\mathrm{r}}(\delta,\tau,\bar{x})=\sum_{i=1}^{N}x_i\,\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) \tag{D.2}$$

and

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}x_i x_j F_{ij}\,\alpha_{ij}^{\mathrm{r}}(\delta,\tau) \tag{D.3}$$

In equation (D.1), the first term on the right-hand side, $\alpha_{\mathrm{o}}^{\mathrm{r}}(\delta,\tau,\bar{x})$, 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 linearly combined using the reduced variables δ and τ of the mixture. The second term is the departure function, $\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$, which is the summation over all binary specific and generalized departure functions. The variables δ and τ are the reduced mixture density and inverse reduced mixture temperature, respectively, as given by

$$\delta=\frac{\rho}{\rho_{\mathrm{r}}(\bar{x})} \tag{D.4}$$

and

$$\tau=\frac{T_{\mathrm{r}}(\bar{x})}{T} \tag{D.5}$$

where

ρ_{r} and T_r are reducing functions for the mixture density and mixture temperature depending on the molar composition of the mixture only (see 4.2.7 and Annex E.1).

D.1.1 Derivatives of the residual part of the reduced Helmholtz free energy

The derivatives of the residual part $\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ of the reduced Helmholtz free energy α of the mixture with respect to the reduced mixture variables δ and τ are as follows:

$$\alpha_{\delta}^{\mathrm{r}}=\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial\delta}\right)_{\tau,\bar{x}}=\sum_{i=1}^{N}x_i\left(\frac{\partial\alpha_{\mathrm{o}i}^{\mathrm{r}}}{\partial\delta}\right)_{\tau}+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}x_i x_j F_{ij}\left(\frac{\partial\alpha_{ij}^{\mathrm{r}}}{\partial\delta}\right)_{\tau} \tag{D.6}$$

$$\alpha_{\delta\delta}^{\mathrm{r}}=\left(\frac{\partial^2\alpha^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau,\bar{x}}=\sum_{i=1}^{N}x_i\left(\frac{\partial^2\alpha_{\mathrm{o}i}^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau}+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}x_i x_j F_{ij}\left(\frac{\partial 2\alpha_{ij}^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau} \tag{D.7}$$

$$\alpha^{\mathrm{r}}_{\delta\tau} = \left(\frac{\partial^2\alpha^{\mathrm{r}}}{\partial\delta\partial\tau}\right)_{\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta\partial\tau}\right) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial^2\alpha^{\mathrm{r}}_{ij}}{\partial\delta\partial\tau}\right) \tag{D.8}$$

$$\alpha^{\mathrm{r}}_{\tau} = \left(\frac{\partial\alpha^{\mathrm{r}}}{\partial\tau}\right)_{\delta,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\tau}\right)_{\delta} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial\alpha^{\mathrm{r}}_{ij}}{\partial\tau}\right)_{\delta} \tag{D.9}$$

$$\alpha^{\mathrm{r}}_{\tau\tau} = \left(\frac{\partial^2\alpha^{\mathrm{r}}}{\partial\tau^2}\right)_{\delta,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\tau^2}\right)_{\delta} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial^2\alpha^{\mathrm{r}}_{ij}}{\partial\tau^2}\right)_{\delta} \tag{D.10}$$

D.2 Calculation of 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 $\alpha^{\mathrm{r}}_{\mathrm{o}}$ to the residual part of the reduced Helmholtz free energy of the mixture is given by equation (D.2), where the residual part of the reduced Helmholtz free energy of component i, $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$, (i.e., the residual part of the respective pure substance equation of state) is given by

$$\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}}\,e^{-\delta^{c_{\mathrm{o}i,k}}} \tag{D.11}$$

For each of the pure substances, the equations for $\alpha^{\mathrm{r}}_{\mathrm{o}i}$ use the same basic structure, however, the number of terms differs. For the main components, the equations consist of 24 terms for methane, nitrogen, and ethane, and of 22 terms for carbon dioxide. For the secondary alkanes and the other secondary components (oxygen, carbon monoxide, hydrogen sulfide, helium, and argon), 12 terms are used, while the equations for hydrogen and water consist of 14 and 16 terms, respectively. The values of the coefficients $n_{\mathrm{o}i,k}$ and exponents $d_{\mathrm{o}i,k}$, $t_{\mathrm{o}i,k}$, and $c_{\mathrm{o}i,k}$ for the 21 components are given in Annex D.2.2.

D.2.1 Derivatives of $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$ with respect to the reduced mixture variables δ and τ

The derivatives of the residual part of the reduced Helmholtz free energy of component i, $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$, (equation (D.11)) with respect to the reduced mixture variables δ and τ are as follows:

$$\begin{aligned}\delta\left(\frac{\partial\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta}\right)_{\tau} = &\sum_{k=1}^{K_{Pol,i}} n_{\mathrm{o}i,k} d_{\mathrm{o}i,k}\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}} \\ &+ \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{\mathrm{o}i,k}\left(d_{\mathrm{o}i,k} - c_{\mathrm{o}i,k}\delta^{c_{\mathrm{o}i,k}}\right)\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)\end{aligned} \tag{D.12}$$

$$\begin{aligned}\delta^2\left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta^2}\right)_{\tau} = &\sum_{k=1}^{K_{Pol,i}} n_{\mathrm{o}i,k} d_{\mathrm{o}i,k}\left(d_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}} \\ &+ \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{\mathrm{o}i,k}\left[\left(d_{\mathrm{o}i,k} - c_{\mathrm{o}i,k}\delta^{c_{\mathrm{o}i,k}}\right)\left(d_{\mathrm{o}i,k}-1-c_{\mathrm{o}i,k}\delta^{c_{\mathrm{o}i,k}}\right) - c^2_{\mathrm{o}i,k}\delta^{c_{\mathrm{o}i,k}}\right]\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)\end{aligned} \tag{D.13}$$

$$\begin{aligned}\delta\tau\left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta\,\partial\tau}\right) = &\sum_{k=1}^{K_{Pol,i}} n_{\mathrm{o}i,k} d_{\mathrm{o}i,k} t_{\mathrm{o}i,k}\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}} \\ &+ \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{\mathrm{o}i,k} t_{\mathrm{o}i,k}\left(d_{\mathrm{o}i,k} - c_{\mathrm{o}i,k}\delta^{c_{\mathrm{o}i,k}}\right)\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)\end{aligned} \tag{D.14}$$

$$\tau\left(\frac{\partial\alpha_{\mathrm{oi}}^{\mathrm{r}}}{\partial\tau}\right)_{\delta}=\sum_{k=1}^{K_{Pol,i}} n_{\mathrm{oi},k}t_{\mathrm{oi},k}\delta^{d_{\mathrm{oi},k}}\tau^{t_{\mathrm{oi},k}} + \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{\mathrm{oi},k}t_{\mathrm{oi},k}\delta^{d_{\mathrm{oi},k}}\tau^{t_{\mathrm{oi},k}}\exp\left(-\delta^{c_{\mathrm{oi},k}}\right) \tag{D.15}$$

$$\tau^{2}\left(\frac{\partial^{2}\alpha_{\mathrm{oi}}^{\mathrm{r}}}{\partial\tau^{2}}\right)_{\delta}=\sum_{k=1}^{K_{Pol,i}} n_{\mathrm{oi},k}t_{\mathrm{oi},k}\left(t_{\mathrm{oi},k}-1\right)\delta^{d_{\mathrm{oi},k}}\tau^{t_{\mathrm{oi},k}} + \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{\mathrm{oi},k}t_{\mathrm{oi},k}\left(t_{\mathrm{oi},k}-1\right)\delta^{d_{\mathrm{oi},k}}\tau^{t_{\mathrm{oi},k}}\exp\left(-\delta^{c_{\mathrm{oi},k}}\right) \tag{D.16}$$

D.2.2 Coefficients and exponents of $\alpha_{\mathrm{oi}}^{\mathrm{r}}(\delta,\tau)$

Table D.1 — Values of the coefficients and exponents in equation (D.11) for methane, nitrogen, and ethane a,b

k	$n_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$
	Methane	**Nitrogen**	**Ethane**
1	0,573 357 042 391 62	0,598 897 118 012 01	0,635 967 804 50714
2	−0,167 606 875 237 30×10^{1}	−0,169 415 574 807 31×10^{1}	−0,173 779 817 854 59×10^{1}
3	0,234 052 918 349 16	0,245 797 361 917 18	0,289 140 609 262 72
4	−0,219 473 763 434 41	−0,237 224 567 551 75	−0,337 142 768 456 94
5	0,163 692 014 041 28×10^{-1}	0,179 549 187 151 41×10^{-1}	0,224 059 646 995 61×10^{-1}
6	0,150 044 063 892 80×10^{-1}	0,145 928 757 202 15×10^{-1}	0,157 154 248 869 13×10^{-1}
7	0,989 904 894 929 18×10^{-1}	0,100 080 659 362 06	0,114 506 342 537 45
8	0,583 827 709 290 55	0,731 571 153 855 32	0,106 120 493 797 45×10^{1}
9	−0,747 868 675 603 90	−0,883 722 723 363 66	−0,128 552 244 394 23×10^{1}
10	0,300 333 028 579 74	0,318 876 602 467 08	0,394 146 307 776 52
11	0,209 855 438 065 68	0,207 664 917 287 99	0,313 909 246 820 41
12	−0,185 901 511 330 61×10^{-1}	−0,193 793 154 541 58×10^{-1}	−0,215 922 771 172 47×10^{-1}
13	−0,157 825 583 390 49	−0,169 366 415 549 83	−0,217 236 665 649 05
14	0,127 167 352 207 91	0,135 468 460 417 01	−0,289 995 744 394 89
15	−0,320 197 438 943 46×10^{-1}	−0,330 667 120 953 07×10^{-1}	0,423 211 730 257 32
16	−0,680 497 293 645 36×10^{-1}	−0,606 908 170 185 57×10^{-1}	0,464 341 002 592 60×10^{-1}
17	0,242 914 128 537 36×10^{-1}	0,127 975 482 928 71×10^{-1}	−0,131 383 983 297 41
18	0,514 404 516 394 44×10^{-2}	0,587 436 641 072 99×10^{-2}	0,114 928 503 643 68×10^{-1}
19	−0,190 849 497 335 32×10^{-1}	−0,184 519 519 719 69×10^{-1}	−0,333 876 884 299 09×10^{-1}
20	0,552 296 772 412 91×10^{-2}	0,472 266 220 424 72×10^{-2}	0,151 831 715 836 44×10^{-1}
21	−0,441 973 929 760 85×10^{-2}	−0,520 240 796 805 99×10^{-2}	−0,476 108 056 476 57×10^{-2}
22	0,400 614 167 084 29×10^{-1}	0,435 635 059 566 35×10^{-1}	0,469 171 662 778 85×10^{-1}
23	−0,337 520 859 075 75×10^{-1}	−0,362 516 907 509 39×10^{-1}	−0,394 017 558 046 49×10^{-1}
24	−0,251 276 582 133 57×10^{-2}	−0,289 740 268 665 43×10^{-2}	−0,325 699 562 476 11×10^{-2}

k	$c_{\mathrm{oi},k}$	$d_{\mathrm{oi},k}$	$t_{\mathrm{oi},k}$		k	$c_{\mathrm{oi},k}$	$d_{\mathrm{oi},k}$	$t_{\mathrm{oi},k}$
1	–	1	0,125		13	2	2	4,5

Table D.1 *(continued)*

k	$n_{\mathrm{o}i,k}$		$n_{\mathrm{o}i,k}$			$n_{\mathrm{o}i,k}$		
2	–	1	1,125		14	2	3	4,75
3	–	2	0,375		15	2	3	5
4	–	2	1,125		16	2	4	4
5	–	4	0,625		17	2	4	4,5
6	–	4	1,5		18	3	2	7,5
7	1	1	0,625		19	3	3	14
8	1	1	2,625		20	3	4	11,5
9	1	1	2,75		21	6	5	26
10	1	2	2,125		22	6	6	28
11	1	3	2		23	6	6	30
12	1	6	1,75		24	6	7	16

[a] The values of the coefficients and exponents are also valid for equation (9).

[b] $K_{\mathrm{Pol},i} = 6$, $K_{\mathrm{Exp},i} = 18$.

Table D.2 — Values of the coefficients and exponents in equation (D.11) for propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, oxygen, carbon monoxide, hydrogen sulfide, and argon[a-c].

k	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$
	Propane	**n-Butane**	**Isobutane**
1	0,104 039 731 073 58×10^{1}	0,106 262 774 114 55×10^{1}	0,104 293 315 891 00×10^{1}
2	−0,283 184 040 814 03×10^{1}	−0,286 209 518 283 50×10^{1}	−0,281 842 725 488 92×10^{1}
3	0,843 938 096 062 94	0,887 382 334 037 77	0,861 762 323 978 50
4	−0,765 595 918 500 23×10^{-1}	−0,125 705 811 553 45	−0,106 136 194 524 87
5	0,946 973 730 572 80×10^{-1}	0,102 863 087 081 06	0,986 157 493 021 34×10^{-1}
6	0,247 964 754 970 06×10^{-3}	0,253 580 406 026 54×10^{-3}	0,239 482 086 823 22×10^{-3}
7	0,277 437 604 228 70	0,323 252 002 339 82	0,303 300 048 569 50
8	−0,438 460 006 483 77×10^{-1}	−0,379 507 610 574 32×10^{-1}	−0,415 981 561 350 99×10^{-1}
9	−0,269 910 647 843 50	−0,325 348 020 144 52	−0,299 919 374 700 58
10	−0,693 134 130 898 60×10^{-1}	−0,790 509 690 510 11×10^{-1}	−0,803 693 427 641 09×10^{-1}
11	−0,296 321 459 816 53×10^{-1}	−0,206 367 205 477 75×10^{-1}	−0,297 613 732 511 51×10^{-1}
12	0,140 401 267 513 80×10^{-1}	0,570 538 093 347 50×10^{-2}	0,130 596 303 031 40×10^{-1}
	n-Pentane	**Isopentane**	**n-Hexane**
1	0,109 686 430 980 01×10^{1}	1,096 3	0,105 532 380 136 61×10^{1}
2	−0,299 888 882 980 61×10^{1}	−3,040 2	−0,261 206 158 906 29×10^{1}
3	0,995 168 867 992 12	1,031 7	0,766 138 829 672 60
4	−0,161 707 085 585 39	−0,154 10	−0,297 703 206 224 59
5	0,113 344 600 727 75	0,115 35	0,118 799 077 333 58
6	0,267 605 951 507 48×10^{-3}	0,000 298 09	0,279 228 610 626 17×10^{-3}
7	0,409 798 819 869 31	0,395 71	0,463 475 898 441 05
8	−0,408 764 230 830 75×10^{-1}	−0,045 881	0,114 331 969 802 97×10^{-1}
9	−0,381 694 824 694 47	−0,358 04	−0,482 569 687 381 31

Table D.2 *(continued)*

k	$n_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$
10	−0,109 319 568 439 93	−0,101 07	−0,937 505 589 246 59×10^{-1}
11	−0,320 732 233 279 90×10^{-1}	−0,035 484	−0,672 732 471 559 94×10^{-2}
12	0,168 770 162 169 75×10^{-1}	0,018 156	−0,511 415 835 854 28×10^{-2}
	n-Heptane	**n-Octane**	**n-Nonane**
1	0,105 437 476 452 62×10^{1}	0,107 225 448 756 33×10^{1}	0,111 51×10^{1}
2	−0,265 006 815 061 44×10^{1}	−0,246 329 511 720 03×10^{1}	−0,270 20×10^{1}
3	0,817 300 478 275 43	0,653 866 740 549 28	0,834 16
4	−0,304 513 912 534 28	−0,363 249 740 856 28	−0,388 28
5	0,122 538 687 108 00	0,127 132 696 267 64	0,137 60
6	0,272 664 727 439 28×10^{-3}	0,307 135 727 779 30×10^{-3}	0,281 85×10^{-3}
7	0,498 658 256 816 70	0,526 568 569 875 40	0,620 37
8	−0,714 328 150 841 76×10^{-3}	0,193 628 628 576 53×10^{-1}	0,158 47×10^{-1}
9	−0,542 368 955 254 50	−0,589 394 268 491 55	−0,617 26
10	−0,138 018 216 107 56	−0,140 699 639 919 34	−0,150 43
11	−0,615 952 873 800 11×10^{-2}	−0,789 663 305 000 36×10^{-2}	−0,129 82×10^{-1}
12	0,486 025 103 930 22×10^{-3}	0,330 365 979 681 09×10^{-2}	0,443 25×10^{-2}
	n-Decane	**Oxygen**	**Carbon monoxide**
1	0,104 61×10^{1}	0,888 782 863 697 01	0,905 54
2	−0,248 07×10^{1}	−0,248 794 333 121 48×10^{1}	−2,451 5
3	0,743 72	0,597 501 907 758 86	0,531 49
4	−0,525 79	0,965 018 170 618 81×10^{-2}	0,024 173
5	0,153 15	0,719 704 287 127 70×10^{-1}	0,072 156
6	0,328 65×10^{-3}	0,223 374 430 001 95×10^{-3}	0,000 188 18
7	0,841 78	0,185 586 863 914 74	0,194 05
8	0,554 24×10^{-1}	−0,381 293 680 357 60×10^{-1}	−0,043 268
9	−0,735 55	−0,153 522 453 830 06	−0,127 78
10	−0,185 07	−0,267 268 149 109 19×10^{-1}	−0,027 896
11	−0,207 75×10^{-1}	−0,256 752 986 771 27×10^{-1}	−0,034 154
12	0,123 35×10^{-1}	0,957 143 021 236 68×10^{-2}	0,016 329
	Hydrogen sulfide	**Argon**	
1	0,876 41	0,850 957 148 039 69	
2	−0,203 67×10^{1}	−0,240 032 229 434 80×10^{1}	
3	0,216 34	0,541 278 414 764 66	
4	−0,501 99×10^{-1}	0,169 197 706 925 38×10^{-1}	
5	0,669 94×10^{-1}	0,688 259 650 190 35×10^{-1}	
6	0,190 76×10^{-3}	0,214 280 328 153 38×10^{-3}	
7	0,202 27	0,174 298 953 219 92	
8	−0,453 48×10^{-2}	−0,336 544 956 041 94×10^{-1}	
9	−0,222 30	−0,135 267 998 576 91	
10	−0,347 14×10^{-1}	−0,163 873 507 915 52×10^{-1}	
11	−0,148 85×10^{-1}	−0,249 876 668 514 75×10^{-1}	

Table D.2 *(continued)*

k	$n_{oi,k}$		$n_{oi,k}$			$n_{oi,k}$		
12	0,741 54$\times10^{-2}$		0,887 692 048 157 09$\times10^{-2}$					
k	$c_{oi,k}$	$d_{oi,k}$	$t_{oi,k}$		k	$c_{oi,k}$	$d_{oi,k}$	$t_{oi,k}$
1	–	1	0,25		7	1	2	0,625
2	–	1	1,125		8	1	5	1,75
3	–	1	1,5		9	2	1	3,625
4	–	2	1,375		10	2	4	3,625
5	–	3	0,25		11	3	3	14,5
6	–	7	0,875		12	3	4	12

[a] The values of the coefficients and exponents are also valid for equation (9).

[b] $K_{\mathrm{Pol},i} = 6$, $K_{\mathrm{Exp},i} = 6$.

[c] For the simultaneously optimized equations of state of Span and Wagner (2003),[10] the old molar gas constant R^* was substituted with the recent one R without conversion. This has nearly no effect on the quality of the equations of state (page 104 of [2]).

Table D.3 — Values of the coefficients and exponents in equation (D.11) for carbon dioxide, hydrogen, water, and helium[a]

k	$c_{oi,k}$	$d_{oi,k}$	$t_{oi,k}$	$n_{oi,k}$
		Carbon dioxide[b]		
1	–	1	0	0,526 465 648 046 53
2	–	1	1,25	−0,149 957 250 425 92$\times10^{1}$
3	–	2	1,625	0,273 297 867 337 82
4	–	3	0,375	0,129 495 000 227 86
5	1	3	0,375	0,154 040 883 418 41
6	1	3	1,375	−0,581 869 509 468 14
7	1	4	1,125	−0,180 224 948 382 96
8	1	5	1,375	−0,953 899 040 728 12$\times10^{-1}$
9	1	6	0,125	−0,804 868 193 176 79$\times10^{-2}$
10	1	6	1,625	−0,355 477 512 730 90$\times10^{-1}$
11	2	1	3,75	−0,280 790 148 824 05
12	2	4	3,5	−0,824 358 900 816 77$\times10^{-1}$
13	3	1	7,5	0,108 324 279 790 06$\times10^{-1}$
14	3	1	8	−0,670 739 931 610 97$\times10^{-2}$
15	3	3	6	−0,468 279 076 005 24$\times10^{-2}$
16	3	3	16	−0,283 599 118 321 77$\times10^{-1}$
17	3	4	11	0,195 001 747 440 98$\times10^{-1}$
18	5	5	24	−0,216 091 375 071 66
19	5	5	26	0,437 727 949 269 72
20	5	5	28	−0,221 307 901 135 93
21	6	5	24	0,151 901 899 573 31$\times10^{-1}$
22	6	5	26	−0,153 809 489 533 00$\times10^{-1}$

Table D.3 *(continued)*

k	$c_{\mathrm{oi},k}$	$d_{\mathrm{oi},k}$	$t_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$
Hydrogen[c]				
1	–	1	0,5	0,535 799 284 512 52×10^{1}
2	–	1	0,625	−0,620 502 525 305 95×10^{1}
3	–	2	0,375	0,138 302 413 270 86
4	–	2	0,625	−0,713 979 548 961 29×10^{-1}
5	–	4	1,125	0,154 740 539 597 33×10^{-1}
6	1	1	2,625	−0,149 768 064 057 71
7	1	5	0	−0,263 687 239 884 51×10^{-1}
8	1	5	0,25	0,566 813 031 560 66×10^{-1}
9	1	5	1,375	−0,600 639 580 304 36×10^{-1}
10	2	1	4	−0,450 439 420 271 32
11	2	1	4,25	0,424 788 402 445 00
12	3	2	5	−0,219 976 408 271 39×10^{-1}
13	3	5	8	−0,104 995 213 745 30×10^{-1}
14	5	1	8	−0,289 559 028 668 16×10^{-2}
Water[d]				
1	–	1	0,5	0,827 284 087 495 86
2	–	1	1,25	−0,186 022 204 165 84×10^{1}
3	–	1	1,875	−0,111 990 096 137 44×10^{1}
4	–	2	0,125	0,156 357 539 760 56
5	–	2	1,5	0,873 758 448 590 25
6	–	3	1	−0,366 744 037 157 31
7	–	4	0,75	0,539 878 934 324 36×10^{-1}
8	1	1	1,5	0,109 576 902 144 99×10^{1}
9	1	5	0,625	0,532 130 378 285 63×10^{-1}
10	1	5	2,625	0,130 505 339 308 25×10^{-1}
11	2	1	5	−0,410 795 204 344 76
12	2	2	4	0,146 374 433 441 20
13	2	4	4,5	−0,557 268 386 237 19×10^{-1}
14	3	4	3	−0,112 017 741 438 00×10^{-1}
15	5	1	4	−0,660 627 580 680 99×10^{-2}
16	5	1	6	0,469 185 220 045 38×10^{-2}
Helium[e]				
1	–	1	0	−0,455 790 240 067 37
2	–	1	0,125	0,125 163 907 549 25×10^{1}
3	–	1	0,75	−0,154 382 316 506 21×10^{1}
4	–	4	1	0,204 674 897 072 21×10^{-1}
5	1	1	0,75	−0,344 762 123 807 81
6	1	3	2,625	−0,208 584 595 127 87×10^{-1}

Table D.3 *(continued)*

k	$c_{\mathrm{oi},k}$	$d_{\mathrm{oi},k}$	$t_{\mathrm{oi},k}$	$n_{\mathrm{oi},k}$
7	1	5	0,125	0,162 274 147 117 78×10^{-1}
8	1	5	1,25	−0,574 718 182 008 92×10^{-1}
9	1	5	2	0,194 624 164 307 15×10^{-1}
10	2	2	1	−0,332 956 801 230 20×10^{-1}
11	3	1	4,5	−0,108 635 773 723 67×10^{-1}
12	3	2	5	−0,221 733 652 459 54×10^{-1}

[a] The values of the coefficients and exponents are also valid for equation (9).

[b] $K_{\mathrm{Pol},i} = 4$, $K_{\mathrm{Exp},i} = 18$.

[c] $K_{\mathrm{Pol},i} = 5$, $K_{\mathrm{Exp},i} = 9$.

[d] $K_{\mathrm{Pol},i} = 7$, $K_{\mathrm{Exp},i} = 9$.

[e] $K_{\mathrm{Pol},i} = 4$, $K_{\mathrm{Exp},i} = 8$.

D.3 Calculation of 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 cases where fitting the parameters of the reducing functions for density and temperature (see Annex E) to accurate experimental data is not sufficient. The departure function $\Delta\alpha^{\mathrm{r}}$ of the multicomponent mixture is the double summation over all binary specific and generalized departure functions developed for the binary subsystems and is given by

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{D.17}$$

with

$$\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x}) = x_i x_j F_{ij}\,\alpha_{ij}^{\mathrm{r}}(\delta,\tau) \tag{D.18}$$

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

$$\alpha_{ij}^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right) \tag{D.19}$$

where

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

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 $\gamma_{ij,k}$ in equation (D.19) for all binary specific and generalized departure functions considered in the mixture model are given in Table D.4. The values of the non-zero F_{ij} parameters in equation (D.18) are listed in Table D.5.

D.3.1 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 (D.18) equals unity.

D.3.2 Generalized departure functions

A generalized departure function was developed for the binary mixtures of methane with either 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).

D.3.3 No departure functions

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

D.3.4 Derivatives of $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ with respect to the reduced mixture variables δ and τ

The derivatives of the function $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ (equation D.19) with respect to the reduced mixture variables δ and τ are as follows:

$$\delta\left(\frac{\partial\alpha_{ij}^{\mathrm{r}}}{\partial\delta}\right)_{\tau} = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} d_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)\left[d_{ij,k} - 2\eta_{ij,k}\,\delta\left(\delta-\varepsilon_{ij,k}\right) - \delta\beta_{ij,k}\right] \tag{D.20}$$

$$\delta^2\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau} = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} d_{ij,k}\left(d_{ij,k}-1\right) \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)\left[\left(d_{ij,k} - 2\eta_{ij,k}\,\delta\left(\delta-\varepsilon_{ij,k}\right) - \delta\beta_{ij,k}\right)^2 - d_{ij,k} - 2\eta_{ij,k}\delta^2\right]$$

(D.21)

$$\delta\tau\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\delta\,\partial\tau}\right) = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} d_{ij,k} t_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} t_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)\left[d_{ij,k} - 2\eta_{ij,k}\,\delta\left(\delta-\varepsilon_{ij,k}\right) - \delta\beta_{ij,k}\right] \tag{D.22}$$

$$\tau\left(\frac{\partial\alpha_{ij}^{\mathrm{r}}}{\partial\tau}\right)_{\delta} = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} t_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} t_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right) \tag{D.23}$$

$$\tau^2\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\tau^2}\right)_\delta = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k}t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}}\tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k}t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}}\tau^{t_{ij,k}}\ \exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)$$

(D.24)

D.3.5 Coefficients, exponents, and parameters for the departure functions

Table D.4 — Values of the coefficients, exponents, and parameters in equation (D.19) for the binary specific and generalized departure functions[a]

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
Methane–Nitrogen[b]							
1	1	0	−0,980 389 855 173 35×10^{-2}	–	–	–	–
2	4	1,85	0,424 872 701 430 05×10^{-3}	–	–	–	–
3	1	7,85	−0,348 002 145 761 42×10^{-1}	1	0,5	1	0,5
4	2	5,4	−0,133 338 130 138 96	1	0,5	1	0,5
5	2	0	−0,119 936 949 746 27×10^{-1}	0,25	0,5	2,5	0,5
6	2	0,75	0,692 433 797 751 68×10^{-1}	0	0,5	3	0,5
7	2	2,8	−0,310 225 081 482 49	0	0,5	3	0,5
8	2	4,45	0,244 954 917 532 26	0	0,5	3	0,5
9	3	4,25	0,223 698 167 169 81	0	0,5	3	0,5
Methane–Carbon dioxide[c]							
1	1	2,6	−0,108 593 873 549 42	–	–	–	–
2	2	1,95	0,802 285 767 273 89×10^{-1}	–	–	–	–
3	3	0	−0,933 039 851 157 17×10^{-2}	–	–	–	–
4	1	3,95	0,409 892 740 058 48×10^{-1}	1	0,5	1	0,5
5	2	7,95	−0,243 380 197 724 94	0,5	0,5	2	0,5
6	3	8	0,238 553 472 811 24	0	0,5	3	0,5
Methane–Ethane[d]							
1	3	0,65	−0,809 260 502 987 46×10^{-3}	–	–	–	–
2	4	1,55	−0,753 819 250 800 59×10^{-3}	–	–	–	–
3	1	3,1	−0,416 187 688 912 19×10^{-1}	1	0,5	1	0,5
4	2	5,9	−0,234 521 736 815 69	1	0,5	1	0,5
5	2	7,05	0,140 038 405 845 86	1	0,5	1	0,5
6	2	3,35	0,632 817 448 077 38×10^{-1}	0,875	0,5	1,25	0,5
7	2	1,2	−0,346 604 258 488 09×10^{-1}	0,75	0,5	1,5	0,5
8	2	5,8	−0,239 187 473 342 51	0,5	0,5	2	0,5
9	2	2,7	0,198 552 550 668 91×10^{-2}	0	0,5	3	0,5
10	3	0,45	0,617 777 461 715 55×10^{1}	0	0,5	3	0,5
11	3	0,55	−0,695 753 582 711 05×10^{1}	0	0,5	3	0,5

Table D.4 *(continued)*

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
12	3	1,95	0,106 301 853 063 88×10^{1}	0	0,5	3	0,5
Methane–Propane[e]							
1	3	1,85	0,137 464 299 585 76×10^{-1}	–	–	–	–
2	3	3,95	−0,744 250 121 295 52×10^{-2}	–	–	–	–
3	4	0	−0,455 166 002 136 85×10^{-2}	–	–	–	–
4	4	1,85	−0,545 466 033 502 37×10^{-2}	–	–	–	–
5	4	3,85	0,236 820 168 244 71×10^{-2}	–	–	–	–
6	1	5,25	0,180 077 637 214 38	0,25	0,5	0,75	0,5
7	1	3,85	−0,447 739 429 324 86	0,25	0,5	1	0,5
8	1	0,2	0,193 273 748 882 00×10^{-1}	0	0,5	2	0,5
9	2	6,5	−0,306 321 978 046 24	0	0,5	3	0,5
Nitrogen–Carbon dioxide[f]							
1	2	1,85	0,286 616 250 283 99	–	–	–	–
2	3	1,4	−0,109 198 338 612 47	–	–	–	–
3	1	3,2	−0,113 740 320 822 70×10^{1}	0,25	0,5	0,75	0,5
4	1	2,5	0,765 805 442 373 58	0,25	0,5	1	0,5
5	1	8	0,426 380 009 268 19×10^{-2}	0	0,5	2	0,5
6	2	3,75	0,176 735 382 045 34	0	0,5	3	0,5
Nitrogen–Ethane[g]							
1	2	0	−0,473 765 181 266 08	–	–	–	–
2	2	0,05	0,489 611 934 610 01	–	–	–	–
3	3	0	−0,570 110 620 905 35×10^{-2}	–	–	–	–
4	1	3,65	−0,199 668 200 413 20	1	0,5	1	0,5
5	2	4,9	−0,694 111 031 017 23	1	0,5	1	0,5
6	2	4,45	0,692 261 927 390 21	0,875	0,5	1,25	0,5
Methane–Hydrogen[h]							
1	1	2	−0,251 571 349 719 34	–	–	–	–
2	3	−1	−0,622 038 411 119 83×10^{-2}	–	–	–	–
3	3	1,75	0,888 503 151 843 96×10^{-1}	–	–	–	–
4	4	1,4	−0,355 922 125 732 39×10^{-1}	–	–	–	–
Methane–n-Butane, Methane–Isobutane, Ethane–Propane, Ethane–n-Butane, Ethane–Isobutane, Propane–n-Butane, Propane–Isobutane, and n-Butane–Isobutane[i]							
1	1	1	0,255 747 768 441 18×10^{1}	–	–	–	–
2	1	1,55	−0,798 463 571 363 53×10^{1}	–	–	–	–
3	1	1,7	0,478 591 314 658 06×10^{1}	–	–	–	–
4	2	0,25	−0,732 653 923 695 87	–	–	–	–
5	2	1,35	0,138 054 713 453 12×10^{1}	–	–	–	–
6	3	0	0,283 496 034 763 65	–	–	–	–
7	3	1,25	−0,490 873 859 404 25	–	–	–	–

Table D.4 *(continued)*

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
8	4	0	−0,102 918 889 214 47	–	–	–	–
9	4	0,7	0,118 363 146 819 68	–	–	–	–
10	4	5,4	$0,555\ 273\ 857\ 219\ 43\times10^{-4}$	–	–	–	–

[a] The values of the coefficients, exponents, and parameters are also valid for equation (12).

[b] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 7$.

[c] $K_{\mathrm{Pol},ij} = 3$, $K_{\mathrm{Exp},ij} = 3$.

[d] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 10$.

[e] $K_{\mathrm{Pol},ij} = 5$, $K_{\mathrm{Exp},ij} = 4$.

[f] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 4$.

[g] $K_{\mathrm{Pol},ij} = 3$, $K_{\mathrm{Exp},ij} = 3$.

[h] $K_{\mathrm{Pol},ij} = 4$, $K_{\mathrm{Exp},ij} = 0$.

[I] $K_{\mathrm{Pol},ij} = 10$, $K_{\mathrm{Exp},ij} = 0$.

Table D.5 — Values of the non-zero F_{ij} parameters in equation (D.18) for the binary specific and generalized departure functionsa,b

Mixture *i*–*j*	F_{ij}
Methane–Nitrogen	1
Methane–Carbon dioxide	1
Methane–Ethane	1
Methane–Propane	1
Methane–n-Butane	1
Methane–Isobutane	0,771 035 405 688
Methane–Hydrogen	1
Nitrogen–Carbon dioxide	1
Nitrogen–Ethane	1
Ethane–Propane	0,130 424 765 150
Ethane–n-Butane	0,281 570 073 085
Ethane–Isobutane	0,260 632 376 098
Propane–n-Butane	$0,312\ 572\ 600\ 489\times10^{-1}$
Propane–Isobutane	$-0,551\ 609\ 771\ 024\times10^{-1}$
n-Butane–Isobutane	$-0,551\ 240\ 293\ 009\times10^{-1}$

[a] The values of the F_{ij} parameters are also valid for equation (11).

[b] The F_{ij} parameters equal zero for all other binary combinations.

Annex E
(normative)

The reducing functions for density and temperature

E.1 Calculation of the reducing functions for density and temperature

The composition-dependent reducing functions are used to calculate the reduced mixture variables δ and τ (i.e., dimensionless mixture density and temperature, respectively) according to

$$\delta = \frac{\rho}{\rho_\mathrm{r}(\bar{x})} \tag{E.1}$$

and

$$\tau = \frac{T_\mathrm{r}(\bar{x})}{T} \tag{E.2}$$

The reducing functions for density and temperature can be written as

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

and

$$T_\mathrm{r}(\bar{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j} \right)^{0.5} \tag{E.4}$$

with

$\beta_{v,ij} = 1/\beta_{v,ji}$, $\gamma_{v,ij} = \gamma_{v,ji}$, $\beta_{T,ij} = 1/\beta_{T,ji}$, and $\gamma_{T,ij} = \gamma_{T,ji}$

These functions are based on quadratic mixing rules and are thus reasonably connected to physically well-founded mixing rules. The binary parameters of equations (E.3) and (E.4) consider the deviation between the behaviour of the real mixture and the one resulting from the ideal combining rules (with β and γ set to 1) for the critical parameters of the pure components.

The values of the binary parameters $\beta_{v,ij}$, $\gamma_{v,ij}$, $\beta_{T,ij}$, and $\gamma_{T,ij}$ in equations (E.3) and (E.4) for all binary mixtures are listed in Table E.1. The critical parameters $\rho_{c,i}$ and $T_{c,i}$ of the pure components are given in Annex C.

E.1.1 Binary parameters for mixtures with no or very poor experimental data

The binary parameters $\beta_{v,ij}$ and $\gamma_{v,ij}$ in equation (E.3) and $\beta_{T,ij}$ and $\gamma_{T,ij}$ in equation (E.4) are fitted to experimental data for binary mixtures. In those cases where sufficient experimental data are not available, the parameters of equations (E.3) and (E.4) 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 that proved to be more suitable for certain binary subsystems. For example, for binary hydrocarbon