BS EN ISO 20765-2:2018

BSI Standards Publication

Natural gas - Calculation of thermodynamic properties

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

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National foreword

This British Standard is the UK implementation of EN ISO 20765-2:2018. It is identical to ISO 20765-2:2015. It supersedes BS ISO 20765-2:2015, which is withdrawn.

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

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

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English Version

Natural gas - Calculation of thermodynamic properties - Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application (ISO 20765-2:2015)

Gaz naturel - Calcul des propriétés thermodynamiques -- Partie 2: Propriétés des phases uniques (gaz, liquide, fluide dense) pour une gamme étendue d'applications (ISO 20765-2:2015)

Erdgas - Berechnung thermodynamischer Eigenschaften - Teil 2: Einphaseneigenschaften (gasförmig, flüssig und dicht-flüssig) für den erweiterten Anwendungsbereich (ISO 20765-2:2015)

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European foreword

The text of ISO 20765-2:2015 has been prepared by Technical Committee ISO/TC 193 "Natural gas" of the International Organization for Standardization (ISO) and has been taken over as EN ISO 20765-2:2018 by Technical Committee CEN/TC 238 "Test gases, test pressures, appliance categories and gas appliance types" the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by March 2019, and conflicting national standards shall be withdrawn at the latest by March 2019.

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Contents

Page

Foreword ... **v**

1 Scope ... **1**

2 Normative references ... **2**

3 Terms and definitions ... **2**

4 Thermodynamic basis of the method ... **4**
4.1 Principle ... 4
4.2 The fundamental equation based on the Helmholtz free energy ... 4
4.2.1 Background ... 4
4.2.2 The Helmholtz free energy ... 5
4.2.3 The reduced Helmholtz free energy ... 5
4.2.4 The reduced Helmholtz free energy of the ideal gas ... 6
4.2.5 The pure substance contribution to the residual part of the reduced Helmholtz free energy ... 6
4.2.6 The departure function contribution to the residual part of the reduced Helmholtz free energy ... 7
4.2.7 Reducing functions ... 8
4.3 Thermodynamic properties derived from the Helmholtz free energy ... 8
4.3.1 Background ... 8
4.3.2 Relations for the calculation of thermodynamic properties in the homogeneous region ... 9

5 Method of calculation ... **11**
5.1 Input variables ... 11
5.2 Conversion from pressure to reduced density ... 11
5.3 Implementation ... 12

6 Ranges of application ... **13**
6.1 Pure gases ... 13
6.2 Binary mixtures ... 14
6.3 Natural gases ... 17

7 Uncertainty of the equation of state ... **18**
7.1 Background ... 18
7.2 Uncertainty for pure gases ... 18
7.2.1 Natural gas main components ... 18
7.2.2 Secondary alkanes ... 19
7.2.3 Other secondary components ... 21
7.3 Uncertainty for binary mixtures ... 21
7.4 Uncertainty for natural gases ... 23
7.4.1 Uncertainty in the normal and intermediate ranges of applicability of natural gas ... 24
7.4.2 Uncertainty in the full range of applicability, and calculation of properties beyond this range ... 25
7.5 Uncertainties in other properties ... 25
7.6 Impact of uncertainties of input variables ... 25

8 Reporting of results ... **25**

Annex A (normative) **Symbols and units** ... **27**

Annex B (normative) **The reduced Helmholtz free energy of the ideal gas** ... **29**

Annex C (normative) **Values of critical parameters and molar masses of the pure components** ... **35**

Annex D (normative) **The residual part of the reduced Helmholtz free energy** ... **36**

Annex E (normative) **The reducing functions for density and temperature** ... **48**

Annex F (informative) **Assignment of trace components** ... **55**

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Annex G (informative) **Examples** **57**
Bibliography **60**

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Full document details: BS EN ISO 20765-2:2018

Foreword

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

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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)*

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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

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.

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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.

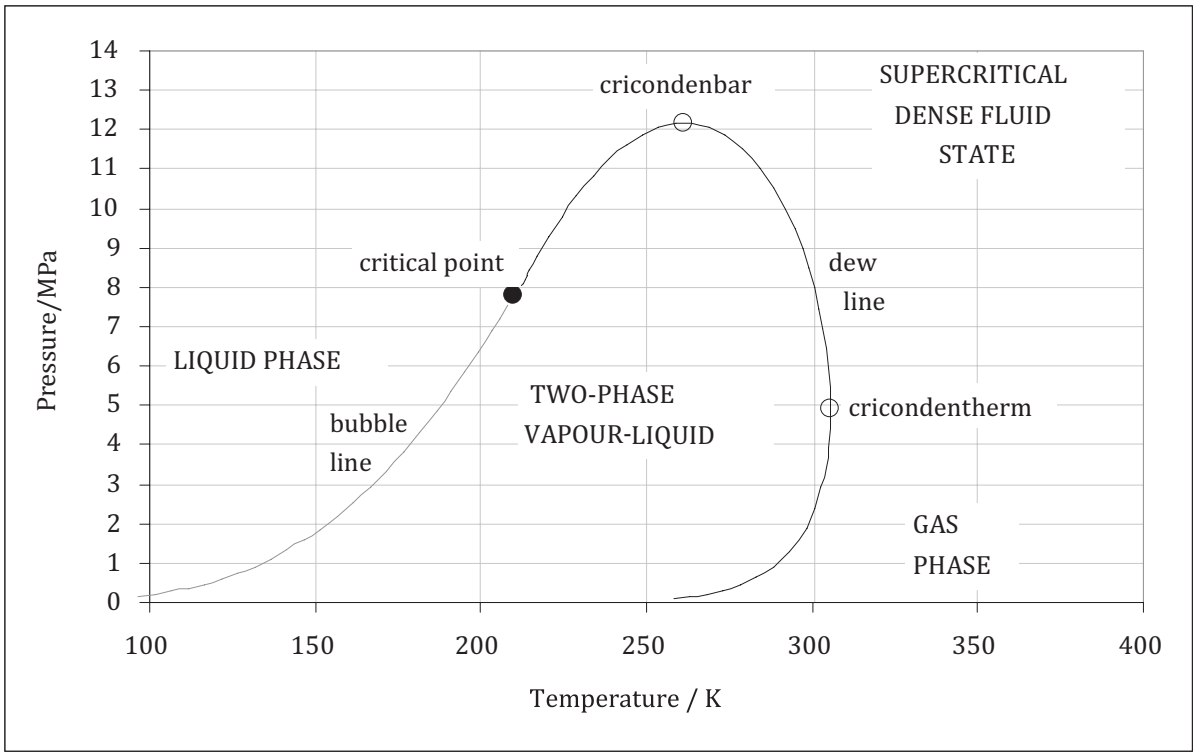

Figure 1 — Phase diagram for a typical natural gas

3.1
bubble pressure
pressure at which an infinitesimal amount of vapour is in equilibrium with a bulk liquid for a specified temperature

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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

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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.

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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)).

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4.2.4 The reduced Helmholtz free energy of the ideal gas

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

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

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

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

where

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

The values of the coefficients $n_{oi,k}^{o}$ and the parameters $\vartheta_{oi,k}^{o}$ for all 21 components are given in Annex B.

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

NOTE 2 R = 8,314 472 J·mol^{-1}·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 J·mol^{-1}·K^{-1} takes into account this difference and therefore leads to the exact solution of the original equations for the ideal-gas heat capacity.

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

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

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

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where

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

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

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

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

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

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

with

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

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

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

where

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

a) **Binary specific departure functions**

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

b) **Generalized departure function**

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

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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

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

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

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

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

4.3 Thermodynamic properties derived from the Helmholtz free energy

4.3.1 Background

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

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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.

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

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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

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

where

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

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 $\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau)$ with respect to δ and the coefficients and exponents involved (see equation (9)) are given in Annex D.2. The derivatives of $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ 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.

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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:

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$$\alpha(\delta,\tau,\bar{x})=\sum_{i=1}^{N}x_i\frac{R^*}{R}\left[n_{\mathrm{o}i,1}^{\mathrm{o}}+n_{\mathrm{o}i,2}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}+n_{\mathrm{o}i,3}^{\mathrm{o}}\ln\left(\frac{T_{\mathrm{c},i}}{T}\right)+\sum_{k=4,6}n_{\mathrm{o}i,k}^{\mathrm{o}}\ln\left|\sinh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right|\right.$$

$$\left.-\sum_{k=5,7}n_{\mathrm{o}i,k}^{\mathrm{o}}\ln\left|\cosh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right|\right]+\sum_{i=1}^{N}x_i\left[\ln\left(\frac{\rho}{\rho_{\mathrm{c},i}}\right)+\ln x_i\right]$$

$$+\sum_{i=1}^{N}x_i\left[\sum_{k=1}^{K_{\mathrm{Pol},i}}n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}}+\sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}}n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\tau^{t_{\mathrm{o}i,k}}e^{-\delta^{c_{\mathrm{o}i,k}}}\right] \tag{36}$$

$$+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}x_ix_jF_{ij}\left[\sum_{k=1}^{K_{\mathrm{Pol},ij}}n_{ij,k}\,\delta^{d_{ij,k}}\tau^{t_{ij,k}}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}}n_{ij,k}\,\delta^{d_{ij,k}}\tau^{t_{ij,k}}e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^2-\beta_{ij,k}(\delta-\gamma_{ij,k})}\right]$$

For all 21 components, the values of the coefficients $n_{\mathrm{o}i,k}^{\mathrm{o}}$ and the parameters $\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}$ of the ideal-gas part of the reduced Helmholtz free energy are given in Annex B. The values of the coefficients $n_{\mathrm{o}i,k}$ and exponents $d_{\mathrm{o}i,k}$, $t_{\mathrm{o}i,k}$, and $c_{\mathrm{o}i,k}$ 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.

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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

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