archives
of thermodynamics
Vol. **41**(2020), No. 4, 23–61
DOI: 10.24425/ather.2020.135853

Development of real gas model operating in gas turbine system in Python programming environment

PAWEŁ TRAWIŃSKI[*]

Warsaw University of Technology, Institute of Heat Engineering,
Nowowiejska 21/25, 00-665, Warsaw, Poland

Abstract Identification of working fluids and development of their mathematical models should always precede construction of a proper model of the analysed thermodynamic system. This paper presents method of development of a mathematical model of working fluids in a gas turbine system and its implementation in Python programming environment. Among the thermodynamic parameters of the quantitative analysis of systems, the following were selected: specific volume, specific isobaric and isochoric heat capacity and their ratio, specific enthalpy and specific entropy. The development of the model began with implementation of dependencies describing the semi-ideal gas. The model was then extended to the real gas model using correction factors reflecting the impact of pressure. The real gas equations of state were chosen, namely due to Redlich–Kwong, Peng–Robinson, Soave–Redlich–Kwong, and Lee–Kesler. All the correction functions were derived analytically from the mentioned equations of real gas behaviour. The philosophy of construction of computational algorithms was presented and relevant calculation and numerical algorithms were discussed. Created software allowed to obtain results which were analysed and partially validated.

Keywords: Mathematical model; Numerical methods; Python; Real gas model; Departure functions

---

[*] Corresponding Author. Email: ptraw@itc.pw.edu.pl

Nomenclature

A, B, C, D – coefficients of cubic or Lee–Kesler equation of state
a, b – characteristic constants in cubic equations of state
a_0, a_1, a_2, a_3, a_4 – coefficients of approximation polynomial for specific isobaric heat capacity
$b_1, b_2, b_3, b_4,$
$c_1, c_2, c_3, c_4, d_1, d_2$ – constants in Lee–Kesler equation of state
C_p – specific isobaric heat capacity
C_v – specific isochoric heat capacity
E – auxiliary function for departure functions of Lee–Kesler equation of state
f – function of acentric factor
h – specific enthalpy
$k_1, k_2, k_3, k_4, k_5, k_6$ – auxiliary constants for departure functions derived from cubic equations of state
M – molar mass
n – molar fraction
p – pressure
R – gas constant
r – auxiliary coefficient for solutions of cubic equation
s – specific entropy
T – thermodynamic temperature
t, w – coefficients of canonical form of cubic equation
u – specific internal energy
V – molar volume
v – specific volume
Z – gas compressibility factor

Greek symbols

α – correction coefficient for cohesive pressure in cubic equations of state
β, γ – coefficients of Lee–Kesler equation of state
Δ – increment or canonical form discriminant
κ – ratio of specific isobaric and isochoric heat capacities
λ – air-fuel equivalence ratio
π – number 3.14
φ, χ, ψ – auxiliary coefficients for calculations of departure functions
ω – acentric factor

Subscripts

$-$ – reference conditions
cr – critical conditions
i – component identification
id – ideal or semi-ideal gas
m – mixture
ref – reference gas
s – simple gas

Abbreviations

EoS	–	equation of state
CSP	–	corresponding states principle
LK	–	Lee–Kesler equation of state
PR	–	Peng–Robinson equation of state
RK	–	Redlich–Kwong equation of state
SRK	–	Soave–Redlich–Kwong equation of state

1 Introduction

Identification of working fluids, analysis of physical model and development of their mathematical model should always precede development and analysis of proper mathematical model of thermodynamic systems and power engineering equipment. In many applications the properties of the working fluids are determined by the ideal gas equation of state and appear to be inaccurate. This applies in particular to applications in areas close to the critical point of the fluid, but also when exposed to high pressures and temperatures. Limits for which the ideal gas equation of state may be a sufficient approximation are defined as 2 MPa and 1473 K for atmospheric air and exhaust gas [1–3]. Advanced mathematical model of working fluid should therefore have a reliable accuracy in a wide range of temperature and pressure. It should also include a change in the thermodynamic properties of the working fluids due to a change in the fractions of the mixture components.

Quantitative analysis of the gas turbine system requires determination of the thermodynamic parameters of the working fluid at characteristic points. Among the most important thermodynamic parameters, the following should be pointed out: specific volume, specific isobaric and isochoric heat capacity and their ratio, specific enthalpy, and specific entropy. In contemporary gas turbine systems it is possible to indicate points where the working fluid parameters are higher than those mentioned above. Furthermore, for a more detailed analysis, variable composition of the working fluids must be taken into account: relative humidity of the atmospheric air directed to the axial compressor, air-fuel equivalence ratio in the combustion process and the mixing of different fluids streams in the expander.

The vast majority of commercially available programs allow to determine thermodynamic parameters with the use of equations of state describing the behaviour of real gases. However, it should be noted that the calculation of deviations for particular thermodynamic parameters (difference between real gas and ideal/semi-ideal gas) is usually performed using numerical methods. This means that components in equations – presented later in this publication: (18), (20), (26), and (31) – expressed by derivatives and integrals, but also solutions of non-linear equations – e.g. presented later in this publication: (36), (46), and (47) – are approximated by iterative numerical methods. As a result, the calculation time of the entire thermal-flow system is extended, especially for issues related to cycle optimisation. It should also be remembered that any approximation of analytical relations by numerical methods leads to distortion of the final results and to a decrease in the accuracy of calculations. What is more, it turns out that using the same mathematical model of gas in different applications (e.g. commercial Aspen Hysys and GateCycle software [4, 5]) leads to discrepancies in the results achieved [6]. The quality of the mathematical model of working fluids ultimately affects the whole quantitative analysis of thermal-flow cycles. Moreover, it is not always possible to modify the composition of mixtures (e.g. natural gas in GateCycle). Programs often rely on libraries of default mixtures that cannot be freely changed in composition. In addition, the determination of pseudocritical parameters for mixtures is usually done in a simplified way, e.g. in GateCycle with the use of Kay's rule. As will be discussed later in this publication, the equations describing real gas are particularly sensitive to the quality of the pseudocritical parameters obtained. Another group of programs are applications based on a grid of limited experimental data. Determination of thermodynamic parameters in points between the points of the extended grid is done by interpolation of values from the nearest points described by experimental data. Lastly, computational modules containing mathematical models can only be used in the environment of which they are part. It is not possible to use them outside of the master software.

Mathematical model was built with the use of equations of state describing the behaviour of real gas. These equations should be as accurate as possible, not difficult to implement and have relatively low calculation costs. From a number of analysed equations of state describing real gas behaviour, the models due to Redlich–Kwong, Peng–Robinson, Soave–Redlich–Kwong, and Lee–Kesler were selected. Those equations provided a foundation for the development of mathematical models of fluids working in a classic gas turbine system. Similar approach and modelling attempts can be found in the literature: [1–3, 7–10]. However, these publications are only concerned with selective equations of state for real gas (e.g. the Berthelot equation of state [1–3], no longer so commonly used) and are mostly based on numerical – not analytical – calculations (e.g. [7]). The only attempts to determine analytical relations focus on one selected gas equation and concern individual selected thermodynamic parameters (e.g. only specific enthalpy or specific entropy) [8–10]. There are no publications which present universal analytical relations for real gas equations with respect to all thermodynamic parameters necessary for a complete description of working fluids (e.g. specific isobaric heat capacity). The vast majority of models are therefore based on numerical calculations, which use general formulas describing thermodynamic parameters. As in the case of specialised software for the modelling of thermal-flow cycles, the models available in the literature refer to numerical methods of calculating integrals and derivatives and solving non-linear equations.

A novelty proposed in this paper is to use fully analytical relations to describe all thermodynamic parameters of real gases. This refers in particular to the pressure correction factors. The universal formulas that can be applied to all cubic equations originating from the van der Waals equation of state were derived analytically. These include equations describing: specific isobaric and isochoric heat capacity and their ratio, specific enthalpy and specific entropy. Therefore, the approximation of the pressure correction factors by numerical methods has been eliminated in order to achieve more accurate results by analytical methods. In addition, the use of all iterative methods has been reduced to the minimum necessary. It is worth noting that also solutions of cubic equations of state are fully analytical using algorithms available in the literature. The rejection of numerical and iterative methods, in addition to the accuracy of the results obtained, should also have a positive impact on calculation costs. The publication therefore describes in detail each subsequent step in the development of the mathematical model, both for ideal/semi-ideal and real gases, with particular consideration of mixtures.

A new solution is also the use of Python programming environment as a tool to create applications [11]. All thermodynamic dependencies, calculation algorithms and numerical methods were implemented in this programming environment. The choice of this language was determined by a number of advantages concerning the possibility of using it and the dynamic development of this tool over the last years. Python is an object-oriented general-purpose programming language. It excels in simplicity, conciseness and intuitiveness. Python allows to create complex applications that are highly computationally efficient due to the language architecture. Moreover, it offers the possibility of integration with other programming environments and is independent of the operating system. Numerous specialist services indicate Python as the second most popular programming tool [12].

2 Mathematical model of the working fluid based on the ideal gas equation of state

2.1 Physical model of ideal and semi-ideal gas

The ideal gas model is a physical model that fulfils a number of conditions [13]:

1) gas particles are constantly in chaotic movement,
2) volume of gas molecules is negligible compared to the volume of the whole gas,
3) there is no interaction between the gas molecules except for repulsion at the moment of collision,
4) collisions of gas particles are perfectly elastic,
5) energy of the gas molecules is distributed evenly over all degrees of freedom of movement of the molecule in accordance with the principle of energy equipartition.

These assumptions indicate the limited applicability of the ideal gas equation of state, as mentioned in the introduction, in particular for conditions significantly deviating from standard conditions:

1) as the pressure increases, the distances between the gas molecules decrease and the intermolecular interactions become more important,
2) as the temperature increases, the collisions of molecules are no longer perfectly elastic,
3) as the temperature decreases, the importance of intermolecular interactions increases, especially around the condensation temperature.

In technical applications the concept of semi-ideal gas is introduced. It is a physical model that satisfies the requirements for ideal gas, although it is extended by the dependency of specific heat capacity and temperature.

2.2 Mathematical model of ideal and semi-ideal gas

2.2.1 Ideal gas equation of state

Ideal gas law is an equation of state that bounds pressure, temperature and molar volume of the ideal gas

$$pV = RT\,. \tag{1}$$

Using the molar mass of the fluid, the specific volume of the ideal gas can be determined in the form of

$$v = \frac{RT}{pM}\,. \tag{2}$$

2.2.2 Specific isobaric heat capacity

Specific isobaric heat capacity is a parameter that determines the amount of heat provided to a unit of substance in an isobaric process in relation to the temperature change of that substance. Specific isobaric heat capacity of ideal gas is constant and independent on other thermodynamic parameters, whereas for semi-ideal gas it depends on gas temperature [14].

Specific isobaric heat capacity is a critical parameter that allows to calculate the remaining thermodynamic parameters of ideal and semi-ideal gas and to develop a complete mathematical model of the working fluid. On the basis of knowledge of the function of specific isobaric heat capacity, other relationships describing thermodynamic parameters of the working fluids can be determined: specific isochoric heat capacity, specific heat capacities ratio, specific enthalpy and specific entropy. For these thermodynamic parameters, the analytical equations resulting from the thermodynamics of ideal and semi-ideal gas can be determined only by the function of specific isobaric heat capacity, temperature and pressure, which will be discussed in detail later in this paper.

There are many models available in the literature which approximate the specific isobaric heat capacity as a function of temperature. However, the use of dependencies describing the entire mixtures of dry atmospheric air, natural gas and stoichiometric exhaust gas was rejected. Models have been implemented as mixtures of individual simple compounds, which allowed to consider variable mass or molar fractions. Functions approximating specific isobaric heat capacities differed in the accuracy of results and the temperature range of application. It is also worth adding that the vast majority of available approximation equations takes into account the influence of atmospheric pressure. The general formula defining specific isobaric heat capacity of a semi-ideal gas can be written as

$$\frac{C_p(T)}{R} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \,. \tag{3}$$

Table 1: Coefficients of approximation polynomials for specific isobaric heat capacity of selected compounds [10, 11].

Compound		a_0	$a_1 \times 10^3$	$a_2 \times 10^6$	$a_3 \times 10^9$	$a_4 \times 10^{12}$	Temperature range, K	Source
Argon	Ar	2.5000	0	0	0	0	50–3000	[10, 11]
Nitrogen	N_2	3.5390	−0.261	0.070	1.5700	−0.9900	50–300	[10]
		3.7250	−1.562	3.208	−1.5540	0.1154	300–1000	[11]
		2.4690	2.467	−1.312	0.3401	−0.0345	1000–3000	[11]
Oxygen	O_2	3.6300	−1.794	6.580	−6.0100	1.7900	50–300	[10]
		3.8370	−3.420	10.990	−10.9600	3.7470	300–1000	[11]
		3.1560	1.809	−1.052	0.3190	−0.0363	1000–3000	[11]
Methane	CH_4	4.5680	−8.975	36.310	−34.0700	10.9100	50–300	[10]
		4.5030	−8.965	37.380	−36.4900	12.2200	300–1000	[11]
		−0.6992	15.310	−7.695	1.8960	−0.1849	1000–3000	[11]
Ethane	C_2H_6	4.2210	−8.782	57.950	−67.2900	25.1100	50–300	[10]
		0.8293	20.750	−7.704	0.8756	0	300–1500	[11]
Carbon dioxide	CO_2	3.2590	1.356	15.020	−23.7400	10.5600	50–300	[10]
		2.2270	9.992	−9.802	5.3970	−1.2810	300–1000	[11]
		3.2470	5.847	−3.412	0.9469	−0.1009	1000–3000	[11]

Three approximation formulas were selected for each compound (two for ethane), which described specific isobaric heat capacity in different temperature ranges. Argon as a noble gas has properties very similar to those of ideal gas (constant specific isobaric heat capacity regardless of temperature).

The analysis of the initially obtained results showed discontinuities and surge in changes of specific isobaric heat capacity at the ends of particular temperature ranges. In order to eliminate them, additional intervals were identified in the neighbourhood of the discussed points. In these areas, the specific isobaric heat capacity was calculated on the basis of two dependencies from adjacent intervals, proportionally to the distance from the end of the interval. Obtained mathematical models of temperature variability cover the range from 50 to 3000 K (to 1500 K for ethane). However, the use of the specific isobaric heat capacity model over such a wide temperature range may raise some doubts. For example, because certain compounds (e.g. hydrocarbons) are not physically existing in such a high temperature range – they decompose. In this case, the interpretation of specific isobaric heat capacity makes no physical sense. The final mathematical model of the working fluids will be limited by the values of the input parameters (temperature and pressure). The boundaries will be determined based on the accuracy of the results in the different ranges of input data and the scope of parameters that can practically be found in the gas turbine systems. Results generated from the computational modules for particular compounds are presented in Figs. 1 and 2.

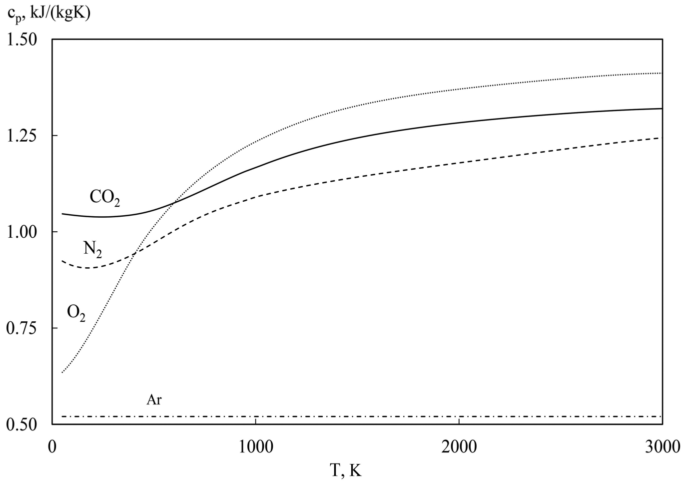

Figure 1: Specific isobaric heat capacity of nitrogen, oxygen, argon and carbon dioxide [14, 15].

Specific isobaric heat capacity of semi-ideal gas is a function that increases with temperature. In these figures, however, it can be observed that in the lowest temperature range for particular compounds (e.g. nitrogen, carbon dioxide, methane) this function reaches its minimum. Further temperature reduction leads to an increase in the specific isobaric heat capacity. This is due to the fact that the implemented approximation equations, although they are solely temperature dependent – Eq. (3), also take

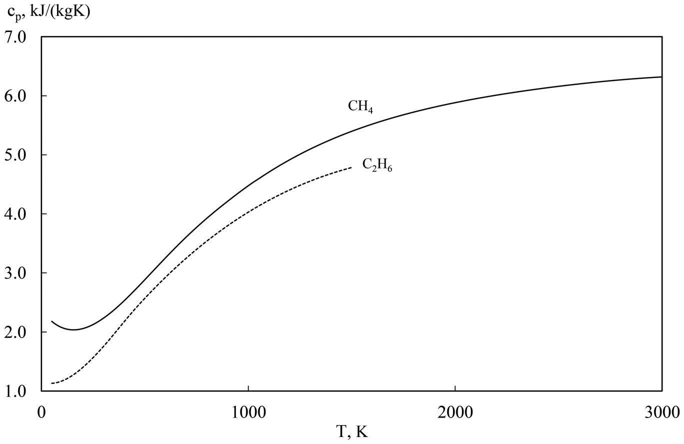

Figure 2: Specific isobaric heat capacity of methane and ethane [14, 15].

into account the effect of atmospheric pressure, as mentioned above. For higher temperatures, the specific isobaric heat capacity models should not vary significantly from the semi-ideal gas model (due to relatively low pressure). The mechanism of influence of pressure on the specific isobaric heat capacity will be discussed in more details in Subsec. 10.1.

2.2.3 Specific isochoric heat capacity

Specific isochoric heat capacity is determined as the amount of heat provided to a unit of substance in an isochoric process in relation to the temperature change of that substance. Similarly to the specific isobaric heat capacity, it should be indicated that for ideal gas it is a constant value independent of other thermodynamic parameters, whereas for semi-ideal gas it is a function of gas temperature. Specific isochoric heat capacity of ideal and semi-ideal gas can be determined using the relation [13]

$$C_v = C_p - R\,. \tag{4}$$

2.2.4 Heat capacity ratio

Heat capacity ratio is a ratio of specific isobaric to specific isochoric heat capacity. It is an important parameter in the analysis of compression and expansion processes of the working fluids in flow systems of thermal machines. For the ideal gas model it depends only on the molecular structure (number of atoms forming a single molecule). Value of the heat capacity ratio can be determined from relation [13]

$$\kappa = \frac{C_p}{C_v}\,. \tag{5}$$

2.2.5 Specific enthalpy

Enthalpy is a sum of internal energy of the system and work done upon environment to create space for this system. Specific enthalpy (related to the unit of substance) can be described as [13]

$$h = u + pV\,. \tag{6}$$

Specific enthalpy of ideal and semi-ideal gas if a function of temperature – it is independent of pressure. Specific enthalpy of ideal gas can be calculated as

$$h = C_p T\,. \tag{7}$$

For semi-ideal gas – after taking into account that specific isobaric heat capacity is a function of temperature:

$$h(T) = \int\limits_0^T C_p(T)\,\mathrm{d}T. \tag{8}$$

In engineering practice, the reference enthalpy values at given temperatures are used. It significantly improves calculations and eliminates the problem of unknown specific isobaric heat capacity function in the entire temperature range

$$h(T) = h_0 + \int\limits_{T_0}^T C_p(T)\,\mathrm{d}T. \tag{9}$$

2.2.6 Specific entropy

Entropy is defined as a measurement of system disorder. It indicates the direction of spontaneous processes in an isolated thermodynamic system. Entropy as a function of state provides information about the irreversibility of thermodynamic processes. Specific entropy of ideal gas can be also related to the reference parameters [13]

$$s = s_0 + C_v \ln\frac{T}{T_0} + R\ln\frac{V}{V_0} \tag{10}$$

or

$$s = s_0 + C_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0}\,. \tag{11}$$

Specific entropy of semi-ideal gas can be obtained by taking into account the variability of specific isobaric and isochoric heat capacities in relation to temperature. In practical calculation tasks (as in the case of specific enthalpy) the values of the reference specific entropy are used

$$s(T) = s_0 + \int_{T_0}^{T} \frac{C_v(T)}{T}\,\mathrm{d}T + R \ln \frac{V}{V_0} \tag{12}$$

or

$$s(T) = s_0 + \int_{T_0}^{T} \frac{C_p(T)}{T}\,\mathrm{d}T - R \ln \frac{p}{p_0}\,. \tag{13}$$

3 Mathematical model of real gas

Dependencies of the discussed thermodynamic parameters are definitely the strongest in relation to the fluid temperature. Relationship between these parameters and pressure is significantly lower and is often neglected in technical applications that require less accuracy.

Advanced mathematical model of dependencies defining real gas was obtained by extending the semi-ideal gas model. The approach of pressure correction factors – functions describing the deviation of the analysed parameters from the ideal gas was applied [1, 3]. This allowed for a transparent presentation of thermodynamic dependencies as a sum of two components: for semi-ideal gas and pressure correction factor for real gas. Pressure correction factors were applied for all thermodynamic parameters, which were discussed for ideal and semi-ideal gas.

3.1 Specific isobaric heat capacity

Specific isobaric heat capacity of real gas can be presented as a sum of two components [1, 3]

$$C_p(p,T) = C_p^{id}(T) + \Delta C_p(p,T). \tag{14}$$

Pressure correction factor for specific isobaric heat capacity is defined as

$$\Delta C_p(p,T) = \int_0^p \left(\frac{\partial C_p}{\partial p}\right)_{T=idem} \mathrm{d}p. \tag{15}$$

Having regard to

$$\left(\frac{\partial C_p}{\partial p}\right)_{T=idem} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p=idem} \tag{16}$$

component related to pressure impact on specific isobaric heat capacity is obtained s

$$\Delta C_p(p,T) = -T\int_0^p \left(\frac{\partial^2 V}{\partial T^2}\right)_{p=idem} \mathrm{d}p. \tag{17}$$

Finally, the original formula can be presented in the form

$$C_p(p,T) = C_p^{id}(T) - T\int_0^p \left(\frac{\partial^2 V}{\partial T^2}\right)_{p=idem} \mathrm{d}p. \tag{18}$$

3.2 Specific isochoric heat capacity

Specific isochoric heat capacity of real gas can be presented as a sum of two components

$$C_v(p,T) = C_v^{id}(T) + \Delta C_v(p,T). \tag{19}$$

Finally, by using thermodynamic relations (similarly as for the specific isobaric heat capacity) the above formula can be presented as [14]

$$C_v(p,T) = C_p^{id}(T) + T\int_0^p \left[\frac{\left(\frac{\partial p}{\partial T}\right)^2_{V=idem}}{\left(\frac{\partial p}{\partial V}\right)_{T=idem}}\right] \mathrm{d}p. \tag{20}$$

3.3 Heat capacity ratio

Heat capacity ratio can be expressed as

$$\kappa(p,T) = \frac{c_p(p,T)}{c_v(p,T)}\,. \tag{21}$$

3.4 Specific enthalpy

Specific enthalpy of real gas can be also presented as a sum of two components [1, 3]

$$h(p,T) = h^{id}(T) + \Delta h(p,T). \tag{22}$$

Pressure correction factor for specific enthalpy is defined as

$$\Delta h(p,T) = \int_0^p \left(\frac{\partial h}{\partial p}\right)_{T=idem} \mathrm{d}p. \tag{23}$$

Having regard to

$$\left(\frac{\partial h}{\partial p}\right)_{T=idem} = V - T\left(\frac{\partial V}{\partial T}\right)_{p=idem} \tag{24}$$

component related to pressure impact on specific enthalpy is obtained as

$$\Delta h(p,T) = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_{p=idem}\right] \mathrm{d}p. \tag{25}$$

Finally, the original formula can be presented in the form

$$h(p,T) = h^{id}(T) + \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_{p=idem}\right] \mathrm{d}p. \tag{26}$$

3.5 Specific entropy

Specific entropy of real gas can be also presented as a sum of two components [1, 3]

$$s(p,T) = s^{id}(T) + \Delta s(p,T). \tag{27}$$

Pressure correction factor for specific entropy is defined as:

$$\Delta s(p,T) = \int_0^p \left(\frac{\partial s}{\partial p}\right)_{T=idem} \mathrm{d}p. \tag{28}$$

Having regard to

$$\left(\frac{\partial s}{\partial p}\right)_{T=idem} = -\left(\frac{\partial V}{\partial T}\right)_{p=idem} \tag{29}$$

component related to pressure impact on specific entropy is obtained as

$$\Delta s(p,T) = -\int_0^p \left(\frac{\partial V}{\partial T}\right)_{p=idem} \mathrm{d}p. \tag{30}$$

Finally, the original formula can be presented in the form:

$$s(p,T) = s^{id}(T) - \int_0^p \left(\frac{\partial V}{\partial T}\right)_{p=idem} \mathrm{d}p. \tag{31}$$

4 Cubic equations of state

Cubic equations of state are equations describing the behaviour of real gas, which derive from the van der Waals equation of state (1873). Common features of this group of equations are the presence of the molar volume in the third power and the characteristic coefficients defining the intermolecular interactions (cohesive pressure) and the volume of the molecules (covolume). Redlich–Kwong, Peng–Robinson, and Soave–Redlich–Kwong equations were chosen to build a mathematical model of working fluids. These cubic equations are also applied in commercial areas.

4.1 Redlich–Kwong equation of state

Redlich–Kwong equation of state (1949) is considered to be the first significant improvement of van der Waals equation of state. It introduces additional empirical relation between cohesive pressure and fluid temperature [16]

$$\left[p + \frac{\alpha}{V(V+b)}\right](V-b) = RT. \tag{32}$$

Correction factor related to the cohesive pressure is a function of the temperature of the working fluid

$$\alpha(T) = \frac{a}{\sqrt{T}}\,. \tag{33}$$

Characteristic constants for Redlich–Kwong equation were determined experimentally depending on the critical parameters of gas:

$$a = 0.427480\frac{R^2T_{cr}^{2.5}}{p_{cr}}\,, \tag{34}$$

$$b = 0.086640\frac{RT_{cr}}{p_{cr}}\,. \tag{35}$$

Redlich–Kwong equation was written as follows due to further considerations and implementation into computational algorithms

$$pV^3 - RTV^2 + \left(\alpha - b^2p - bRT\right)V - \alpha b = 0. \tag{36}$$

4.2 Soave–Redlich–Kwong equation of state

Soave–Redlich–Kwong equation of state (1972) is a modification of Redlich–Kwong equation of state (32). Correction factor related to the cohesive pressure, which is a function of the temperature of the working fluid, was extended by the dependence on acentric factor of the gas molecule [17]

$$\alpha(T) = a\left[1 + f(\omega)\left(1 - \sqrt{\frac{T}{T_{cr}}}\right)\right]^2, \tag{37}$$

where

$$f(\omega) = 0.48508 + 1.54171\omega - 0.15613\omega^2. \tag{38}$$

Characteristic constants for Soave–Redlich–Kwong equation were determined experimentally depending on the critical parameters of gas:

$$a = 0.427480\frac{R^2T_{cr}^2}{p_{cr}}\,, \tag{39}$$

$$b = 0.086640\frac{RT_{cr}}{p_{cr}}\,. \tag{40}$$

Soave–Redlich–Kwong equation was written in identical form as Redlich–Kwong equation (36) due to further considerations and implementation into computational algorithms.

4.3 Peng–Robinson equation of state

Peng–Robinson equation of state (1976) is another improvement of van der Waals equation [18]

$$\left(p + \frac{\alpha}{V^2 + 2bV - b^2}\right)(V - b) = RT. \tag{41}$$

Correction factor related to the cohesive pressure, similarly to the Soave–Redlich–Kwong equation, is dependent on the temperature of the fluid and acentric factor of the gas molecules

$$\alpha = a\left[1 + f(\omega)\left(1 - \sqrt{\frac{T}{T_{cr}}}\right)\right]^2, \tag{42}$$

where

$$f(\omega) = 0.37464 + 1.54226\omega - 0.2699\omega^2. \tag{43}$$

Characteristic constants for Peng–Robinson equation were determined experimentally depending on the critical parameters of gas

$$a = 0.45724\frac{R^2T_{cr}^2}{p_{cr}}, \tag{44}$$

$$b = 0.07780\frac{RT_{cr}}{p_{cr}}. \tag{45}$$

Peng–Robinson equation was written as follows due to further considerations and implementation into computational algorithms

$$pV^3 + (bp - RT)\,TV^2 + \left(\alpha - 3b^2p - 2bRT\right)V + b^2p - \alpha b + b^2RT = 0. \tag{46}$$

5 Corresponding states principle equations of state

This is a group of equations of state based on corresponding states principle (CSP). It postulates that different gases behave identically while being exposed to the same reduced parameters (pressure, temperature, molar volume) [14]. The most popular CSP-based equations of state include Benedict-Webb-Rubin and Lee–Kesler equations.

5.1 Lee–Kesler equation of state

Lee–Kesler equation of state (1975) is a modification of empirical equation of state by Benedict–Webb–Rubin (1940). General form of equation can be written as [19]

$$Z = \left(\frac{p_r V_r}{T_r}\right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right). \quad (47)$$

Coefficients of Lee–Kesler equation of state are given as

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}\,, \quad (48)$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}\,, \quad (49)$$

$$D = d_1 + \frac{d_2}{T_r}\,, \quad (50)$$

and the values of the constants are given in Table 2.

Table 2: Constants in Lee–Kesler equation of state [19].

Constant	Simple fluids	Reference fluids
b_1	0.1181193	0.2026579
b_2	0.2657280	0.3315110
b_3	0.1547900	0.0276550
b_4	0.0303230	0.2034880
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0	0.0169010
c_4	0.0427240	0.0415770
$d_1 \times 10^4$	0.1554880	0.4873600
$d_2 \times 10^4$	0.6236890	0.0740336
β	0.6539200	1.2260000
γ	0.0601670	0.0375400

Compressibility factor of a real gas is a combination of compressibility factors of simple and reference gases. Solving Lee–Kesler equation of state requires the twofold solution of non-linear equation (47) with constants for simple and reference gases. Finally, obtained results are included in relation

$$Z = Z^s + \frac{\omega}{\omega^{ref}} \left(Z^{ref} - Z^s \right), \tag{51}$$

where acentric factor of a reference gas

$$\omega^{ref} = 0.3978. \tag{52}$$

6 Mixing rules

Considering multicomponent mixtures requires establishing appropriate rules of calculating pseudocritical parameters such as pressure, temperature, specific volume, compressibility factor and acentric factor. These rules should also include calculations of equivalent characteristic constants and coefficients for real gas equations of state applied to mixtures. There are numerous approaches for calculations of pseudocritical parameters. It was decided to use the relations detailed in [14]:

$$T_{cr} = \sum n_i T_{cri}\,, \tag{53}$$

$$Z_{cr} = \sum n_i Z_{cri}\,, \tag{54}$$

$$V_{cr} = \sum n_i V_{cri}\,, \tag{55}$$

$$p_{cr} = \frac{Z_{cr} R T_{cr}}{V_{cr}}\,, \tag{56}$$

$$\omega_m = \sum n_i \omega_i\,. \tag{57}$$

For calculations of equivalent constants and coefficients for real gas equations of state for multicomponent mixtures it is recommended to use a combination of geometric (coefficient α) and linear (constant b) approach [16–18].

$$\alpha = \sum_i \sum_j n_i n_j \sqrt{\alpha_i \alpha_j}\,, \tag{58}$$

$$b = \sum_i n_i b_i\,. \tag{59}$$

Calculations of pseudocritical parameters should be carried out in a careful manner. Otherwise, incorrectly obtained values may have a decisive influence on the accuracy of calculations based on real gas equations of state.

This is due to the fact that the characteristic parameters of real gas equations of state are directly dependent on the values of critical parameters: Eqs.: (34), (35), (37)–(40), (42)–(45), and (47). Imprecise determination of pseudocritical temperature and pressure may lead to distortion of the results and consequently to significant errors in the calculations. This applies in particular to calculations related to the pseudocritical pressure of the mixture, which in most commercial programs (e.g. GateCycle) is calculated on the basis of the Kay's rule. It turns out that more accurate results for real gas mixtures can be obtained using relation (56).

7 Departure functions

Based on the general real gas model defined in section 3 and the respective real gas equations of state discussed in sections 4 and 5, analytical relations for pressure correction factors were developed. They are a measurement of the deviation of the behaviour of real gas and semi-ideal gas.

7.1 Departure functions determined using cubic equations of state

The general form of the cubic equation with the use of the compressibility factor of the real gas can be written as

$$Z^3 + AZ^2 + BZ + C = 0, \tag{60}$$

where equation coefficients are defined as:

$$A = \frac{-RT - bp + k_1 p + k_2 p}{RT}, \tag{61}$$

$$B = \frac{-RTk_2 p + \alpha p - bk_2 p^2 + k_1 k_2 p^2 + k_3 p^2}{R^2 T^2}, \tag{62}$$

$$C = \frac{-RTk_3 p^2 - \alpha b p^2 + \alpha k_1 p^2 - bk_3 p^3 + k_1 k_3 p^3}{R^3 T^3}. \tag{63}$$

Characteristic constants and coefficients for particular real gas equations of state are discussed in Sec. 4. Values of the auxiliary coefficients for departure functions are presented in Table 3.

Table 3: Characteristic constants and coefficients for real gas equations of state and auxiliary coefficients for departure functions.

Parameters	Redlich–Kwong	Soave–Redlich–Kwong	Peng–Robinson
α	$\frac{a}{\sqrt{T}}$	$a\left[1+f(\omega)\left(1-\sqrt{\frac{T}{T_{cr}}}\right)\right]^2$	$a\left[1+f(\omega)\left(1-\sqrt{\frac{T}{T_{cr}}}\right)\right]^2$
$f(\omega)$	–	$0.48508+1.54171\omega-0.15613\omega^2$	$0.37464+1.54226\omega-0.2699\omega^2$
a	$0.427480\frac{R^2T_{cr}^{2.5}}{p_{cr}}$	$0.427480\frac{R^2T_{cr}^2}{p_{cr}}$	$0.45724\frac{R^2T_{cr}^2}{p_{cr}}$
b	$0.086640\frac{RT_{cr}}{p_{cr}}$	$0.086640\frac{RT_{cr}}{p_{cr}}$	$0.07780\frac{RT_{cr}}{p_{cr}}$
k_1	0	0	0
k_2	b	b	$2b$
k_3	0	0	$-b^2$
k_4	b	b	b
k_5	0	0	$b\left(\sqrt{2}-1\right)$
k_6	$-b$	$-b$	$-b\left(\sqrt{2}+1\right)$

Moreover, certain auxiliary coefficients were defined for the calculations:

$$\varphi=\sqrt{k_2^2-4k_3}\,, \tag{64}$$

$$\chi=\frac{\varphi+\dfrac{2RTZ}{p}+k_2}{-\varphi+\dfrac{2RTZ}{p}+k_2}\,, \tag{65}$$

$$\psi=\frac{-4\varphi Rp\left[T\left(\dfrac{\partial Z}{\partial T}\right)_{p=idem}+Z\right]}{\left[2RTZ-p\left(\varphi-k_2\right)\right]^2}\,. \tag{66}$$

Algebraic transformations allowed to obtain general formulas for the departure functions for cubic equations of state.

7.1.1 Specific isobaric heat capacity

$$\begin{aligned}\Delta C_p(p,T)=RT\left(\frac{\partial Z}{\partial T}\right)_{p=idem}+R(Z-1)+T\frac{\ln\chi}{\varphi}\frac{d^2\alpha}{dT^2}\\ +\frac{\chi\psi}{\varphi}\left(T\frac{d\alpha}{dT}-\alpha\right).\end{aligned} \tag{67}$$

7.1.2 Specific isochoric heat capacity

$$\Delta C_v(p,T) = T\frac{\ln\chi}{\varphi}\frac{d^2\alpha}{dT^2}\,. \tag{68}$$

7.1.3 Specific enthalpy

$$\Delta h(p,T) = pV - RT + \frac{\alpha - T\dfrac{d\alpha}{dT}}{k_5 - k_6}\ln\left(\frac{V-k_5}{V-k_6}\right)\,. \tag{69}$$

7.1.4 Specific entropy

$$\Delta s(p,T) = R\ln\left[\frac{p}{RT}(V-k_4)\right] - \frac{\dfrac{d\alpha}{dT}}{k_5-k_6}\ln\left(\frac{V-k_5}{V-k_6}\right)\,. \tag{70}$$

7.2 Departure functions determined using CSP-based equations of state

For Lee–Kesler equation of state departure functions defining the influence of pressure on subsequent thermodynamic parameters and the order of calculations are given directly in [19]. Additional relations include:

1) auxiliary function

$$E = \frac{c_4}{2T_r^3\gamma}\left[\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right], \tag{71}$$

2) partial derivative of pressure with respect to temperature at constant volume

$$\left(\frac{\partial p_r}{\partial T_r}\right)_{V_r=idem} = \frac{1}{V_r}\left\{1 + \frac{b_1 + \dfrac{b_3}{T_r^2} + \dfrac{2b_4}{T_r^3}}{V_r} + \frac{c_1 - \dfrac{2c_3}{T_r^3}}{V_r^2} + \frac{d_1}{V_r^5}\right.$$
$$\left. - \frac{2c_4}{T_r^3V_r^2}\left[\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right]\right\}, \tag{72}$$

3) partial derivative of pressure with respect to volume at constant temperature

$$\left(\frac{\partial p_r}{\partial V_r}\right)_{T_r=idem} = -\frac{T_r}{V_r^2}\left\{1+\frac{2B}{V_r}+\frac{3C}{V_r^2}+\frac{6D}{V_r^5}\right.$$
$$\left. -\frac{c_4}{T_r^3V_r^2}\left[3\beta+\left(5-2\left(\beta+\frac{\gamma}{V_r^2}\right)\right)\frac{\gamma}{V_r^2}\right]\exp\left(-\frac{\gamma}{V_r^2}\right)\right\}. \tag{73}$$

7.2.1 Specific isobaric heat capacity

$$\Delta C_p(p,T) = R\left[\frac{2\left(b_3+\dfrac{3b_4}{T_r}\right)}{T_r^2V_r}-\frac{3c_3}{T_r^3V_r^2}-6E-1-T_r\frac{\left(\dfrac{\partial p_r}{\partial T_r}\right)^2_{V_r=idem}}{\left(\dfrac{\partial p_r}{\partial V_r}\right)_{T_r=idem}}\right]. \tag{74}$$

7.2.2 Specific isochoric heat capacity

$$\Delta C_v(p,T) = R\left[\frac{2\left(b_3+\dfrac{3b_4}{T_r}\right)}{T_r^2V_r}-\frac{3c_3}{T_r^3V_r^2}-6E\right]. \tag{75}$$

7.2.3 Specific enthalpy

$$\Delta h(p,T) = RT\left(Z-1-\frac{b_2+\dfrac{2b_3}{T_r}+\dfrac{3b_4}{T_r^2}}{T_rV_r}-\frac{c_2-\dfrac{3c_3}{T_r^2}}{2T_rV_r^2}+\frac{d_2}{5T_rV_r^5}+3E\right). \tag{76}$$

7.2.4 Specific entropy

$$\Delta s(p,T) = R\left(\ln Z-\frac{b_1+\dfrac{b_3}{T_r^2}+\dfrac{2b_4}{T_r^3}}{V_r}-\frac{c_1-\dfrac{2c_3}{T_r^3}}{2V_r^2}-\frac{d_1}{5V_r^5}+2E\right). \tag{77}$$

Determining pressure correction factors for Lee–Kesler equation requires the twofold solution of equation of state – with parameters for simple and reference gas. The final stage is the use of relation (51), which in a similar way allows to determine all departure functions, e.g. for specific enthalpy

$$\Delta h = \Delta h^s + \frac{\omega}{\omega^{ref}}\left(\Delta h^{ref}-\Delta h^s\right). \tag{78}$$

8 Calculation algorithms and numerical methods

Calculation algorithms of the program required the implementation of own functions using the necessary numerical methods. They were collected in a separate calculation module. The chosen numerical methods are discussed below. Detailed description of the implemented numerical methods and theoretical background can be found in the literature, e.g. [20, 21].

8.1 Solving cubic equations

The algorithm of analytical solution of cubic equations is based on calculating the value of the discriminant of the canonical form and examining the existence of real solutions. Implemented function uses values at successive powers of the unknown variable as an input – hence the algebraic transformations of the equations in Sec. 4. The output value is the solution of the equation – specific volume. General form of cubic equations of state can be written in a form

$$AV^3 + BV^2 + CV + D = 0. \tag{79}$$

The first step is to determine the canonical form coefficients of the cubic equation.

$$t = \frac{C}{A} - \frac{B^2}{3A^2}\,, \tag{80}$$

$$w = \frac{2B^3}{27A^3} + \frac{D}{A} - \frac{BC}{3A^2}\,. \tag{81}$$

It is possible to determine the value of the discriminant of canonical form

$$\Delta = \frac{t^2}{4} + \frac{w^3}{27}\,. \tag{82}$$

Then the existence of real solutions of the equation should be examined. Depending on the value of the canonical form discriminant (t and w coefficients) three cases are considered:

1) $\Delta > 0$ – there is only one real solution (the other two roots are complex numbers):

$$V = \sqrt[3]{-\frac{w}{2} + \sqrt{\Delta}} + \sqrt[3]{-\frac{w}{2} - \sqrt{\Delta}} - \frac{B}{3A}\,, \tag{83}$$

2) $t = 0$ and $w = 0$ ($\Delta = 0$) – there is one real solution (triple root)

$$V = -\sqrt[3]{\frac{D}{A}}\,, \tag{84}$$

3) $\Delta < 0$ – there are three different real solutions (the final solution is chosen as the maximum of the three obtained roots):

$$r = \arccos\left(\frac{-\dfrac{w}{2}}{\sqrt{-\dfrac{t^3}{27}}}\right), \tag{85}$$

$$V^{(1)} = 2\sqrt{\frac{-t}{3}}\cos\left(\frac{r}{3}\right) - \frac{B}{3A}\,, \tag{86}$$

$$V^{(2)} = 2\sqrt{\frac{-t}{3}}\cos\left(\frac{r+2\pi}{3}\right) - \frac{B}{3A}\,, \tag{87}$$

$$V^{(3)} = 2\sqrt{\frac{-t}{3}}\cos\left(\frac{r+4\pi}{3}\right) - \frac{B}{3A}\,. \tag{88}$$

8.2 Solving non-linear equations

Algorithms for numerical solving of non-linear equations are based on iterative methods of bisection and Fibonacci (golden-section search) [20, 21]. It is also possible to use other optimisation algorithms (e.g. Newton–Raphson [20, 21]). Selected methods require the determination of: an equation transformed in such a way that all the expressions are on one side, the start and end point of the solution-searching interval, the desired calculation accuracy (bisection method) or the number of iterations (Fibonacci method). Moreover, according to Bolzan–Cauchy's theorem, the starting and ending point of interval should be chosen in such a way that the value of the function at these points has opposite signs [20, 21]. Then it is guaranteed that inside this interval the continuous function has at least one root. Algorithms of iterative solving of non-linear equations were used especially to solve the Lee–Kesler equation of state. Another application are the reverse functions, which calculate the temperature on the basis of pressure and specific enthalpy or specific entropy. Algorithms for solving non-linear equations can also be used for other equations.

8.3 Numerical integration

Two most popular and intuitive methods were used for numerical calculations of integrals: rectangular and trapezoidal methods. Implemented calculation algorithms require specifying the input data: subintegral function, integration interval endpoint, interval discretisation step and reference point. Integration is performed forwards or backwards from the reference point, depending on the value of the endpoint. Algorithms of numerical integration were used especially for calculations of specific enthalpy and entropy of a semi-ideal gas. The reference point is a chosen temperature and reference value is the corresponding specific enthalpy or specific entropy at that temperature.

8.4 Discretisation of the interval and integration step

Discretisation of the intervals were performed using calculation algorithms based on equal division. A list of nodal points was determined with the use of start and end point of the interval and the discretisation step.

Algorithm for determining the integration step was also based on the method of division into equal parts. Calculations required definition of the start and end point of the interval and the desired division multiplication factor. The last parameter specifies on how many parts one unit of the interval length needs to be divided into, e.g. if the required division multiplication factor is set to 100, each single unit of the interval length will be divided 100 times.

Algorithms related to the discretisation of intervals were used mostly as auxiliary algorithms for calculations of numerical integration.

9 Calculation program

9.1 Additional assumptions

Physicochemical constants (molar masses, critical temperatures and pressures, acentric factors and others) as well as specific enthalpies and entropies of reference for particular components were assumed according to the data available in literature and thermodynamic tables [14, 15].

Properties and thermodynamic parameters of water and steam were calculated on the basis of publications of the International Association for the Properties of Water and Steam (IAPWS) [22]. Approximation equations cover the range: 0–1073 K for pressures up to 100 MPa and 1073–2273 K for pressures up to 50 MPa. Steam was considered as one of the components of humid atmospheric air and exhaust gas.

Molar and mass fractions of particular components of working fluids mixtures were obtained according to the thermodynamics of wet gas (humid atmospheric air) and stoichiometry of combustion process (exhaust gas) [13]. Properties of mixtures were calculated according to equations describing ideal and semi-ideal gas mixtures [13, 23].

9.2 Architecture of the program

Calculation program was divided into separate modules according to the working fluid:

1) dry and humid atmospheric air,
2) high-methane natural gas,
3) exhaust gas.

In addition a separate module for water and steam properties was developed based on the mentioned IAPWS publications. All numerical methods and computational algorithms (e.g. algorithm for solving cubic equations) were also collected in a separate computing module.

Functions calculating thermodynamic properties require the temperature and pressure of the working fluid as input data. Reverse functions, which determine the temperature of the fluid on the basis of pressure and specific enthalpy or specific entropy, were also implemented. Each function requires the specification of fractions of particular components and equation of state.

9.3 Exemplary calculations

The philosophy of program was illustrated by an example. The purpose is to calculate specific enthalpy of dry atmospheric air as a real gas with defined parameters of pressure and temperature. Calculations for the properties of natural gas and exhaust gas are carried out in a similar way. Following steps illustrate the calculation process inside the called function.

Step 1: Loading the input parameters of pressure and temperature.

Step 2: Checking if the given parameters do not exceed the limits of the developed mathematical model of the working fluid properties.

Step 3: Identification of mass or molar fractions of the particular components of dry air as a gas mixture.
In this case nitrogen, oxygen and argon were taken into account. For calculations related to humid atmospheric air or exhaust gas, mass fractions are determined on the basis of relative humidity/moisture content and air-fuel equivalence ratio, respectively. Program also allows to manually determine mass fractions of particular components as an optional input data vector.

Step 4: Determination of reference temperature, T_0 and corresponding specific enthalpy, h_0 of dry atmospheric air. The values of specific enthalpies of reference for particular components were taken from literature and available thermodynamic tables. Specific enthalpy of reference for dry atmospheric air mixture was obtained as for ideal gas mixture: as sum of products of mass fractions and specific enthalpies of reference of particular mixture components.

Step 5: Calculation of the integration step on the basis of the temperature range (from the reference temperature to the temperature given in the input parameters) and the required division multiplication factor (the default value is 10 – each unit of the interval length is divided into 10 equal parts).

Step 6: Defining the subintegral function as an auxiliary internal function. For specific enthalpy the proper subintegral function is specific isobaric heat capacity, $C_p(T)$.

Step 7: Calculation of the specific enthalpy of dry atmospheric air as a semi-ideal gas, $h^{id}(T)$, by numerical integration in one of three intervals. For an input temperature lower than the reference temperature backward integration, for an input temperature higher than the reference temperature forward integration. For an input temperature equal to the reference temperature, the integral value is zero.

Step 8: Consideration of the pressure impact, $\Delta h(p,T)$, based on the selected equation of state. For the case of the Clapeyron equation, the pressure impact is equal to zero and no calculations are performed in this step. For the Redlich–Kwong, Soave–Redlich–Kwong, and Peng–Robinson equations of state following properties are determined:

1) specific volume on the basis of chosen equation of state,

2) characteristic constants and coefficients α and b of particular components and whole mixture,

3) auxiliary coefficients k_5 and k_6 and partial derivative $\dfrac{d\alpha}{dT}$,
4) departure function $\Delta h(p,T)$ – pressure correction factor.

For LK equation of state following properties are determined:

1) pseudocritical temperature T_{cr} and pressure p_{cr} of dry atmospheric air mixture,
2) reduced temperature T_r and pressure p_r of dry atmospheric air,
3) specific volume in pseudocritical conditions v_{cr},
4) characteristic coefficients of Lee–Kesler equation of state B^s, C^s, D^s for simple gas,
5) reduced specific volume V_r^s for simple gas as a solution of Lee–Kesler equation,
6) auxiliary function E^s for simple gas,
7) departure function of specific enthalpy Δh^s for simple gas,
8) characteristic coefficients of Lee–Kesler equation of state B^{ref}, C^{ref}, D^{ref} for reference gas,
9) reduced specific volume V_r^{ref} for reference gas as a solution of Lee–Kesler equation,
10) auxiliary function E^{ref} for reference gas,
11) departure function of specific enthalpy Δh^{ref} for reference gas,
12) acentric factor ω of dry atmospheric air mixture,
13) departure function $\Delta h(p,T)$ – pressure correction factor.

Step 9: Calculation of specific enthalpy at given conditions as a sum of: specific enthalpy of semi-ideal gas, $h^{id}(T)$, and departure function – pressure correction factor, $\Delta h(p,T)$, for real gas. Parameters can be expressed in mass (default) or molar.

Step 10: Return of the calculated value.

10 Results

Developed calculation modules were used to determine thermodynamic properties of the working fluids of a gas turbine system. The impact of pressure, temperature, fractions of particular components of the mixture and chosen equation of state were studied. For dry atmospheric air, the results obtained with calculation modules were compared with available experimental data.

10.1 Specific isobaric heat capacity of dry atmospheric air

Values of specific isobaric heat capacity for dry atmospheric air obtained from program were compared with experimental data [20]. Calculations were performed for levels of pressure 0.1, 0.5, 1, 2, and 3 MPa for all implemented equations of state. Differences between each model equation and experimental data were represented by the mean square error (Table 4).

Table 4: Mean square error for results obtained with different equations of state.

Pressure, MPa	Mean square error					Number of points
	IG	RK	PR	SRK	LK	
0.1	0.0197	0.0164	0.0166	0.0165	0.0170	65
0.5	0.0519	0.0167	0.0195	0.0194	0.0174	62
1.0	0.0966	0.0197	0.0245	0.0258	0.0172	60
2.0	0.2370	0.0310	0.0299	0.0471	0.0170	58
3.0	0.3858	0.0170	0.0721	0.0643	0.0307	56

Results indicate unambiguously that as the pressure increases, the semi-ideal gas model generates more significant errors. Among the real gas models, Redlich–Kwong and Lee–Kesler equations present high accuracy in a wide range of parameters. However, it should be noted that the model based on the Lee–Kesler equation requires considerably more mathematical operations. Models based on the Peng–Robinson and Soave–Redlich–Kwong equations become less accurate as the pressure increases.

Specific isobaric heat capacity for the low pressure range indicates a behaviour similar to that of semi-ideal gas; it is a function that generally increases with temperature – Fig. 3. However, as the working fluid pressure increases, its influence on this thermodynamic parameter is noticeable. This is particularly the case in the low temperature range, and as the temperature increases, the pressure impact decreases. Such behaviour can be explained by reference to the basic principles of thermodynamics. As the pressure increases, the distances between the gas molecules decrease, which results directly in an increased role of intermolecular interactions. The equations describing the real gas reflect the influence of the intermolecular interactions directly through the characteristic coefficients for each of them (cubic equations derived from the van der Waals equation of state). Significant values of intermolecular interactions lead to an increase in the amount of heat that has to be supplied to the gas to increase its kinetic energy (absolute temperature) – hence the increased specific isobaric heat capacity, especially in the low temperature range, where the kinetic energy of the molecules is much lower. As the temperature increases, the kinetic energy of the gas molecules also increases. Therefore, an additional further increase in pressure no longer has a significant effect on this value and the effect of pressure on the specific isobaric heat capacity ceases to hold a significant role.

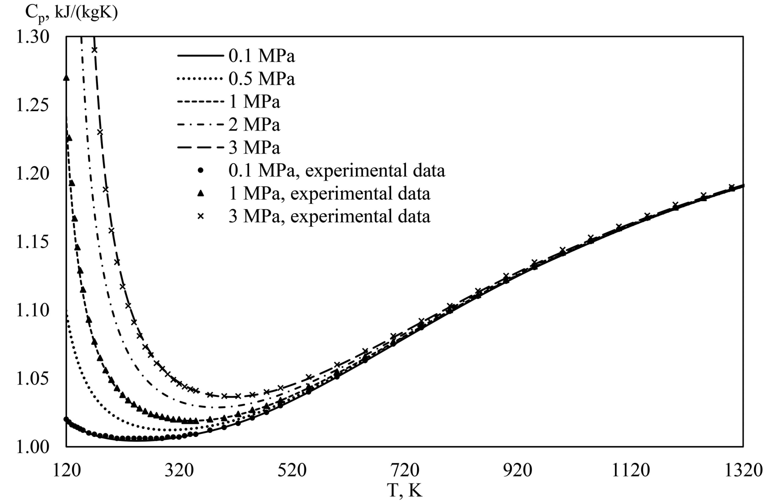

Figure 3: Specific isobaric heat capacity of dry atmospheric air (RK EoS).

The obtained curves of specific isobaric heat capacity for dry atmospheric air for particular pressure levels correspond very adequately to the experimental data [24]. The empirical values are located on successive model data lines corresponding to the subsequent pressure levels.

10.2 Specific isobaric heat capacity of exhaust gas

Values of specific isobaric heat capacity for exhaust gas obtained from program were compared at different levels of air-fuel equivalence ratio. Model based on Lee–Kesler equation of state was used for this comparison. Figure 4 includes also values for the specific isobaric heat capacity of dry atmospheric air.

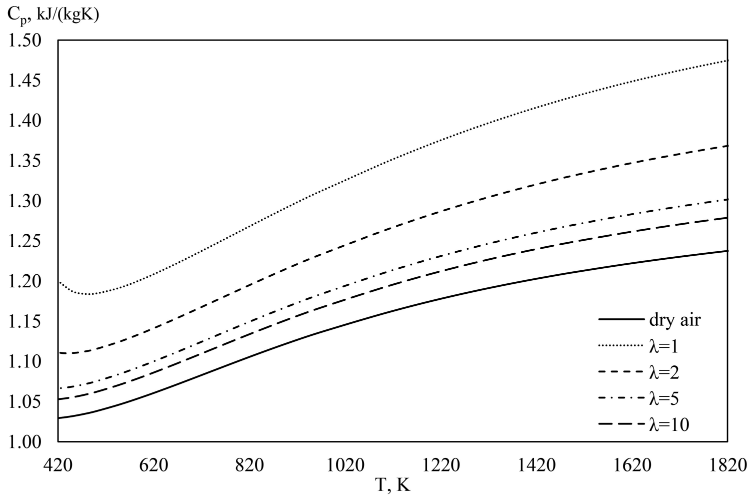

Figure 4: Specific isobaric heat capacity of exhaust gas at different levels of air-fuel equivalence ratio (LK EoS; 2 MPa).

Specific isobaric heat capacity of the exhaust gas increases with the temperature, similar to dry atmospheric air. It is noteworthy that with the increase of the air-fuel equivalence ratio for exhaust gas, the properties of this working fluid approach those of dry atmospheric air in the same conditions. As the air-fuel equivalence ratio increases, the proportion of air to the stoichiometric exhaust gas also increases, therefore: fractions of the particular components of exhaust gas mixture approach those of the corresponding dry atmospheric air components.

10.3 Specific enthalpy of high-methane natural gas

Impact of pressure on specific enthalpy is illustrated with the example of high-methane natural gas in Fig. 5. Study analysed the results generated by the model based on the ideal gas equation and the models based on the real gas equations. For the considered case the pressure of the fluid was set at 5 MPa.

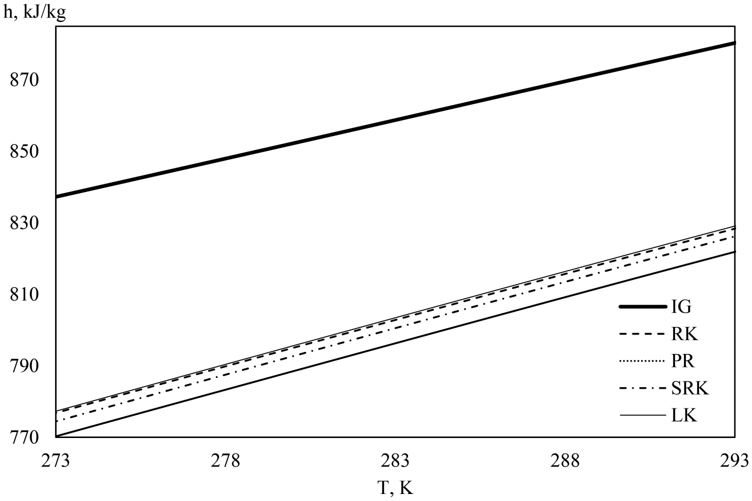

Figure 5: Specific enthalpy of high-methane natural gas (5 MPa).

A narrower temperature range was used to show the differences between particular real gas models. The most significant difference can be seen between the semi-ideal gas model and the real gas models. Distance between each real gas model and the semi-ideal gas model illustrate the impact of pressure on the specific enthalpy of high-methane natural gas resulting from the applied equation of state.

For the semi-ideal gas model, specific enthalpy is a function of the fluid temperature only – Eqs. (8) and (9). Calculation in this case comes down only to the integration of the specific isobaric heat capacity function in a given temperature range for semi-ideal gas. Gas model based on the equations describing the real gas introduces a pressure correction factor illustrating the effect of pressure – Eq. (26), which occurs in addition to the part responsible for integrating the specific isobaric heat capacity function of semi-ideal gas. Taking into account the influence of pressure at constant temperature reduces the specific enthalpy of the working fluid, as can be seen in Fig. 5. This may seem to be in contradiction with Figs. 3 and 4 – an increase in pressure causes an increase in specific isobaric heat capacity, which should also result in an increase in the sum of these values (specific enthalpy). However, it should be noted that for the real gas model, the specific isobaric heat capacity function at a given pressure (e.g. 5 MPa) is not being integrated but the function describing the semi-ideal gas (pressure independent) is. The value of the pressure correction factor in Eq. (26) takes negative values, which results from the values of the subintegral expression – so the specific enthalpy of the real gas will be equal to the specific enthalpy of the semi-ideal gas reduced by the value of this coefficient reflecting the effect of pressure. As the pressure increases, the distances between the molecules decrease, leading to an increase in intermolecular interactions. The increase in the energy of the intermolecular interactions reduces the amount of heat that can be used from the working medium. Therefore, an increase in the pressure will result in a decrease in the specific enthalpy of the working fluid.

10.4 Specific entropy of humid atmospheric air

The impact of the fractions of particular components on the values of thermodynamic parameters of mixture was illustrated on the example of humid atmospheric air in Fig. 6. For different levels of relative humidity the value of specific entropy was studied. Model based on Peng–Robinson equation of state was used for this comparison.

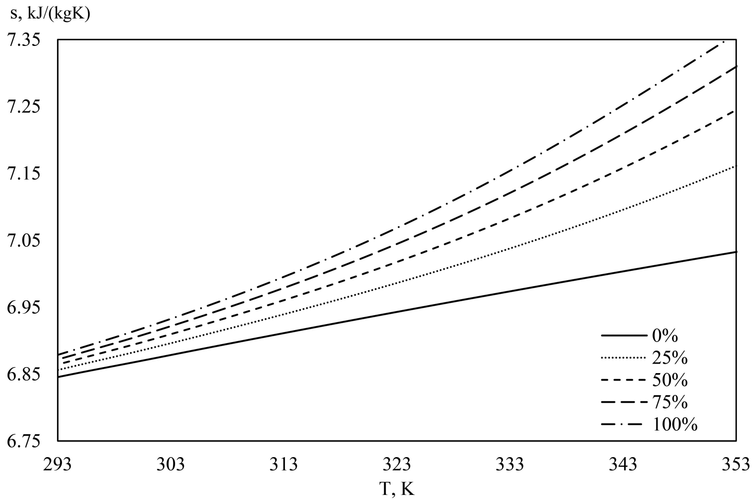

Figure 6: Specific entropy of humid atmospheric air (PR EoS; 0.1 MPa).

As the water vapour content of the humid air mixture increases, the value of specific entropy also increases. The increasing content of water vapour visibly affects the value of thermodynamic properties of the whole mixture.

The fraction of water vapour in the atmospheric air is one of many factors that affect the performance of gas turbine systems. The variable relative humidity value should therefore not be ignored in detailed analyses of the performance of axial compressors and expanders. The increasing fraction of water vapour content in the stream of air taken into the system results directly in thermodynamic parameters of the working fluid at characteristic points of thermal-flow cycle.

11 Summary and conclusions

Developed program allows to determine the thermodynamic parameters of working fluids in a gas turbine system. For a classic system, these are: humid atmospheric air, high-methane natural gas, and exhaust gas. The basic parameters necessary for quantitative analysis of thermodynamic systems were included: specific volume, specific isobaric and isochoric heat capacity and their ratio, specific enthalpy, and specific entropy.

The program started with the implementation of dependencies defining the semi-ideal gas model. This allowed to describe mentioned thermodynamic properties in function of temperature. In order to obtain more accurate results, it was decided to include the impact of pressure. For this purpose, a wide range of equations describing the behaviour of real gas were analysed. The cubic equations of state by Redlich–Kwong, Peng–Robinson and Soave–Redlich–Kwong, and based on the corresponding states principle the Lee–Kesler equation of state were finally chosen.

On the basis of relations defining thermodynamic properties of real gas, general forms of pressure correction factors were determined. They represented the impact of pressure. Then, using the selected real gas equations of state, the departure functions were determined fully analytically.

Therefore, the semi-ideal gas model (dependence of thermodynamic properties on temperature) was extended to the real gas model (additional pressure influence). All relationships for the real gas model were determined fully analytically. This reduced calculation time and improved the accuracy of the results compared to approach where integration and differentiation operations are performed numerically.

Moreover, the variability of fractions of particular components of the mixtures was also included (relative humidity/moisture content in humid atmospheric air, and air-fuel equivalence ratio for exhaust gas). Thermodynamic properties of mixtures were determined on the basis of thermodynamics of semi-ideal gas mixtures. The use of real gas equations of state required additional clarification of the methods of calculating pseudocritical parameters (pressure, temperature, acentric factor, characteristic coefficients of equations of state).

Results generated in the program were analysed and partially validated. Above all, the results obtained for dry atmospheric air were compared with experimental data available in the literature. The accuracy of the results was estimated on the basis of mean square error. The most accurate for this case were Redlich–Kwong and Lee–Kesler equations of state. However, it should be noted that the second one involves a significantly higher number of mathematical operations. Impact of pressure on thermodynamic properties of all indicated working fluids was also analysed. Additionally, the impact of relative humidity and air-fuel equivalence ratio on thermodynamic properties of humid atmospheric air and exhaust gas, respectively, was studied.

On the basis of the obtained accuracy of the results of the mathematical model and the values of the input parameters which can be encountered in the gas turbine systems, it was decided to determine the limits of the input temperature and pressure. It should be noted that for extremely high temperatures certain compounds do not exist physically (as mentioned in subsection 2.1.2), which implies difficulties in the physical interpretation of thermodynamic parameters (e.g. specific isobaric heat capacity). Moreover, extremely high and low values, both for temperature and pressure, do not occur in the thermal-flow cycles of gas turbine systems. The particular mathematical models of working fluids are therefore recommended to be used in range:

1) dry atmospheric air – pressure: 0.05–5 MPa, temperature: 120–1770 K,
2) humid atmospheric air – pressure: 0.05–5 MPa, temperature: 120–1770 K,
3) high-methane natural gas – pressure: 0.05–5 MPa, temperature: 220–770 K,
4) exhaust gas – pressure: 0.05–5 MPa, temperature: 350–2270 K.

Calculations made outside these ranges may result in higher calculation errors. Special attention should also be paid to the possibility of condensation. A suitable example is the mathematical model of exhaust gas. The minimum temperature is the temperature of the dew point defined by the mass fraction of water vapour, which results directly in the partial pressure of this component and the possibility of condensation.

An important element of the program is the module that contains the calculation algorithms of the numerical and computational methods. It turned out to be necessary to implement functions solving cubic and non-linear equations, methods of numerical integration and differentiation, as well as interval discretisation and integration step calculation. Gathering numerical methods in a separate calculation module allows to maintain clarity of the calculation code and allows to use implemented algorithms in other modules of the program or as an independent stand-alone application.

The use of Python programming environment allowed to create a very efficient computing program. The architecture of the language and the way the memory is utilized make the implemented computing code effective and fast. In addition, the language syntax allows for intuitive and efficient development of computing code by the user. Python's features make it possible to create software independent of the operating system. Moreover, such a program can also operate as an extension to other applications, including commercial software. The calculations are made quickly and precisely. Complex calculation algorithms and threads are handled effectively. This is decisive for the analysis and optimisation of thermal-flow systems, where the thermodynamic parameters of the working fluid are calculated at numerous independent points.

All relationships describing thermodynamic parameters of real gas were derived in the analytical way. The proposed universal relationships for pressure correction factors of all thermodynamic parameters (specific isobaric and isochoric heat capacity and their ratio, specific enthalpy and specific entropy) allow the use of any cubic equation of state of real gas. The number of iterative and numerical operations has been reduced to a minimum. In combination with the advantages of Python described above, it allowed to develop a program characterized by high accuracy of results while minimizing calculation costs.

Program can be used as a stand-alone application or as part of larger software. The purpose of the developed application is to support modelling of gas turbine systems. It can also be used for all types of technologies based on the combustion of natural gas. Moreover, the way of implementing the calculation algorithms allows to expand modules and functions with new working fluids. Application can become the foundation for the development of working fluid models for other thermodynamic systems.

Received 29 April 2020

References

[1] Chmielniak T.: Problems of Turbomachinery: working fluids. Vapour and gas thermodynamic cycles. Skrypty Uczelniane Politechniki Śląskiej **695**, Silesian University of Technology, Gliwice 1977 (in Polish).

[2] Badyda K., Miller A.: *Gas turbines and systems of their utilisation for power engineering*. Kaprint, Lublin 2014 (in Polish).

[3] Wark K.: *Thermodynamics*. MacGraw-Hill Book Comp., New York 1988.

[4] https://www.aspentech.com/en/products/engineering/aspen-hysys/ (accessed on: 27 Nov. .2020).

[5] http://www.wyattllc.com/GateCycle/GateCycle.html (accessed on: 27 Nov. 2020).

[6] Zuming L., Iftekhar A. K.: *Simulating combined cycle gas turbine power plants in Aspen HYSYS*. Energ. Convers. Manage. **171**(2018), 1213–1225.

[7] Trawiński P.: *Development and implementation of mathematical models of working mediums for gas part of combined cycle gas turbine system in Python programming environment*. E3S Web Conf., XIV Research & Development in Power Engineering (RDPE 2019), **137**(2019).

[8] Sado J.: *One- dimensional real gas flow*. Bull. Heat Technol. Inst. Warsaw University of Technology **86**(1999), 3–37 (in Polish).

[9] Nederstiggt P.: *Real gas thermodynamics and the isentropic behaviour of substances*. Delft University of Technology, 2017.

[10] Mak P.: *Thermodynamic properties from cubic equations of state*. University of British Columbia Library, Vancouver 1988.

[11] https://docs.python.org/3/ (accessed on: 27 Nov. 2020).

[12] https://octoverse.github.com/ (accessed on: 27 Apr. 2020).

[13] Staniszewski B.: *Termodynamics*. PWN, Warsaw 1989 (in Polish).

[14] Poling B., Prausnitz J., O'Connell J.: *The Properties of Gases and Liquids*. McGraw-Hill, Boston 2007.

[15] Chhabra R. (Ed.): *CRC Handbook of Thermal Engineering* (2nd Edn.). CRC/Taylor&Francis, Boca Raton; London; New York 2018.

[16] Redlich O., Kwong J.: *On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions*. Chem. Rev. **44**(1949), 1, 233–244.

[17] Soave G.: *Equilibrium constants from a modified Redlich–Kwong equation of state*. Chem. Eng. Sci. **27**(1972), 1197–1203.

[18] Peng D., Robinson D.: *A new two-constant equation of state*. Ind. Eng. Chem. Fund. **15**(1976), 59–64.

[19] Lee B., Kesler M.: *A generalized thermodynamic correlation based on three-parameter corresponding states*. AIChE J. **21**(1975), 510–527.

[20] Łukaszewicz J., Warmus M.: *Numerical and graphical methods. Part 1*. Warsaw University of Technology, Warszawa 2010 (in Polish).

[21] Fortuna Z.: *Numerical methods*. PWN, Warszawa 2017 (in Polish).

[22] IAPWS, *Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam*. The International Association for the Properties of Water and Steam, Lucerne 2007.

[23] Litke B.: *Properties of ideal and sem-ideal gases*. Problems of Fundamental Sciences **4**(2016), 95–106 (in Polish).

[24] Vargaftik N.: *Handbook of Physical Properties of Liquids and Gases*. Science, Moscow 1972 (in Russian).