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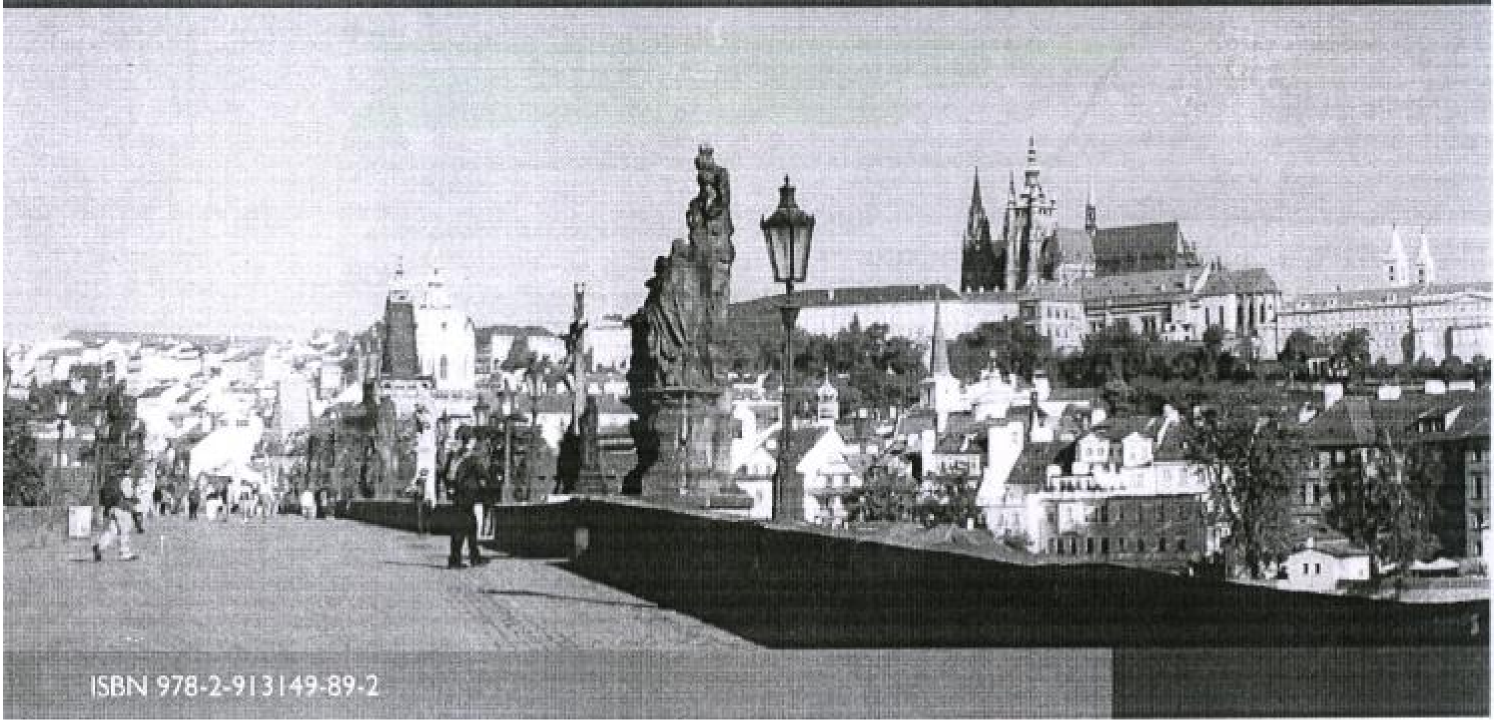

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THE SPECIFIC HEAT AT CONSTANT PRESSURE EVALUATION METHOD FOR COMPUTATION OF THERMODYNAMIC PROPERTIES OF GASES BY MEANS OF LEE – KESLER METHOD

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ABSTRACT

Estimation of thermodynamic properties of gas mixtures using modified Benedict–Webb–Rubin equation by means of the Lee-Kesler method has known advantages over other methods. Mixture parameters, such as specific heat, enthalpy, entropy are estimated by summation of values of these parameters at ideal gas condition and corrections. Analytic dependences for enthalpy and entropy corrections are known. The specific heat at constant pressure correction relates to enthalpy correction by differential dependence, therefore it requires to use numerical methods to evaluate the specific heat correction. Computational formula for the specific heat at constant pressure correction has been obtained by solving this differential equation. Comparison between values of gas mixture basic thermodynamic parameters estimated using obtained formula and values estimated by other methods showed acceptable agreement for engineering computations.

1. INTRODUCTION

The industry and various process technologies requirements define the necessity of evaluating of thermodynamic properties of pure gases and multicomponent mixtures. It is necessary to know thermal and caloric properties for the heat engine, pipeline and other calculations, for estimating of the thermal loading of equipment, power consumption, heat loss and others.

The experimental estimation of the thermodynamic properties of substances is very time and resource consuming. There are experimental data for many pure gases, but the experimental data for gas mixtures are quite limited at the present time. Therefore the task of estimating of the thermodynamic properties of specified composition gas mixtures on the basis of the available experimental data (without implementation of special experiments) continues to be relevant.

It is desirable to have analytical dependences for the ease of automatization of gas mixtures thermal and caloric properties computation. The obtaining of the relation for the specific heat at constant pressure isothermal correction is presented in section 3.

2. THE ESTIMATION OF THERMODYNAMIC PROPERTIES OF GAS MIXTURES

According to the Lee-Kesler method, which is based on the use of the modified Benedict–Webb–Rubin (BWR) equation, the thermodynamic parameters are estimated by the formula

$$A = A^{bs} + \frac{\omega}{\omega^{rs}} \cdot (A^{rs} - A^{bs}) \tag{1}$$

where A = estimated parameter, ω = acentric factor.

The parameters for the "basic" substance ($\omega = 0$) and for the reference substance are designated by indexes ^{bs} and ^{rs} respectively. N-octane was chosen as the reference substance; $\omega^{rs} = 0{,}3978$. The thermodynamic parameters such as compressibility factor z, isothermal corrections for the specific enthalpy $\Delta i = i - i^{id}$, specific entropy $\Delta s = s - s^{id}$, specific heat at constant pressure $\Delta c_p = c_p - c_p^{id}$ and others are calculated from eq. (1).

The modified BWR equation is

$$\frac{p_r}{T_r \cdot \rho_r} = 1 + B \cdot \rho_r + C \cdot \rho_r^2 + D \cdot \rho_r^5 + \frac{c_4}{T_r^3} \cdot \rho_r^2 \cdot (\beta + \gamma \cdot \rho_r^2) \cdot e^{-\gamma \cdot \rho_r^2}, \tag{2}$$

where reduced state parameters of the considered substance are designated by index $_r$.

The coefficients in the eq. (2) are estimated by formulas

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}, \; C = c_1 - \frac{c_2}{T_r} - \frac{c_3}{T_r^3}, D = d_1 + \frac{d_2}{T_r}. \tag{3}$$

The reduced density is $\rho_r = \frac{p_r}{z \cdot T_r}$, therefore eq. (2) can be represented in the form, which is more convenient for the calculation of z by means of the step-by-step approach:

$$z = 1 + B \cdot \frac{p_r}{T_r \cdot z} + C \cdot (\frac{p_r}{T_r})^2 \cdot \frac{1}{z^2} + D \cdot (\frac{p_r}{T_r})^5 \cdot \frac{1}{z^5} + \frac{c_4}{T_r^3} \cdot (\frac{p_r}{T_r})^2 \cdot \frac{1}{z^2} \cdot \left[\beta + \gamma \cdot (\frac{p_r}{T_r})^2 \cdot \frac{1}{z^2}\right] \cdot e^{-\gamma (\frac{p_r}{T_r})^2 \frac{1}{z^2}}. \tag{4}$$

z^{bs} for the "basic" substance and z^{rs} for the reference substance are calculated according to the eq. (4). Then z for the considered substance are calculated using eq. (1). The corrections for the enthalpy, specific heat at constant pressure and entropy are calculated similarly.

The values of critical parameters for more than 400 substances are presented by Reid *et al.* (1977). The values of coefficients for "basic" and reference substances are presented by Zagoruchenko *et al.* (1980). The dependences for acentric factor calculation are presented also in mentioned above works.

The caloric parameters of gas mixture are estimated as the sum of parameter value at the ideal gas condition and the value of corresponding correction. For example, the enthalpy of gas mixture is $i = i^{id} + \Delta i$, where the enthalpy correction is calculated from eq. (1):

$$\begin{aligned} \frac{\Delta i}{R \cdot T_{cr}} &= T_r \cdot z - T_r - \left[b_2 + \frac{2 \cdot b_3}{T_r} + \frac{3 \cdot b_4}{T_r^2}\right] \cdot \rho_r - \left[c_2 - \frac{3 \cdot c_3}{T_r^2}\right] \cdot \frac{\rho_r^2}{2} + \\ &+ \frac{d_2}{5} \cdot \rho_r^5 + \frac{3 \cdot c_4}{2 \cdot T_r^2 \cdot \gamma} \left[\beta + 1 - \left(\beta + 1 - \gamma \cdot \rho_r^2\right) \cdot e^{-\gamma \cdot \rho_r^2}\right]. \end{aligned} \tag{5}$$

The isothermal correction for the specific heat at constant pressure is

$$\frac{\Delta c_p}{R} = \left[\frac{\partial}{\partial T_r}\left(\frac{\Delta i}{R T_{cr}}\right)\right]_{p_r}. \tag{6}$$

The entropy correction is calculated by the formula (Reid *et al.*, 1977)

$$\begin{aligned} \frac{\Delta s}{R} &= \ln \frac{p^{id}}{p} + \ln z - \left(b_1 + \frac{b_3}{T_r^2} + \frac{2 \cdot b_4}{T_r^3}\right) \cdot \rho_r - \left(c_1 - \frac{2 \cdot c_3}{T_r^3}\right) \cdot \frac{\rho_r^2}{2} - \\ &- \frac{d_1}{5} \cdot \rho_r^5 + \frac{c_4}{T_r^3 \cdot \gamma} \cdot \left[\beta + 1 - \left(\beta + 1 + \gamma \cdot \rho_r^2\right) \cdot e^{-\gamma \cdot \rho_r^2}\right]. \end{aligned} \tag{7}$$

If the gas condition changes from initial to final the specific enthalpy change is calculated by equation

$$i_f - i_i = \left[\left(\frac{\Delta i}{R\cdot T_{cr}}\right)_f - \left(\frac{\Delta i}{R\cdot T_{cr}}\right)_i\right]\cdot R\cdot T_{cr} + \int_{T_i}^{T_f} c_p^{id}\cdot dT. \tag{8}$$

If the gas condition changes from initial to final the specific entropy change is calculated by equation

$$s_f - s_i = \left[\left(\frac{\Delta s}{R}\right)_f - \left(\frac{\Delta s}{R}\right)_i\right]\cdot R + \int_{T_i}^{T_f} c_p^{id}\cdot\frac{dT}{T}. \tag{9}$$

3. THE ESTIMATION OF THE SPECIFIC HEAT AT CONSTANT PRESSURE ISOTHERMAL CORRECTION

The dependence for the specific heat at constant pressure isothermal correction is estimated by differentiation of the eq. (5):

$$\begin{aligned}\frac{\Delta c_p}{R} = \left(\frac{\partial I}{\partial T_r}\right)_p &= z - 1 + T_r\cdot\left(\frac{\partial z}{\partial T_r}\right)_p - \left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot\left(b_2 + \frac{2b_3}{T_r} + \frac{3b_4}{T_r^2}\right) - \rho_r\cdot\left(-\frac{2b_3}{T_r^2} - \frac{6\cdot b_4}{T_r^3}\right) - \\ &- \rho_r\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot\left(c_2 - \frac{3c_3}{T_r^2}\right) - \frac{\rho_r^2}{2}\cdot\frac{2\cdot 3\cdot c_3}{T_r^3} + d_2\cdot\rho_r^4\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p + \\ &+ \frac{3\cdot c_4}{2\cdot T_r^2\cdot\gamma}\cdot\left[(2\cdot\rho\cdot\gamma)\cdot e^{-\gamma\rho_r^2}\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot e^{-\gamma\rho_r^2} + \left(\beta + 1 + \gamma\cdot\rho_r^2\right)\cdot e^{-\gamma\rho_r^2}\cdot(-2\rho_r\cdot\gamma)\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p\right] - \\ &- \frac{3\cdot c_4}{T_r^3\cdot\gamma}\cdot\left[\beta + 1 - \left(\beta + 1 + \gamma\cdot\rho_r^2\right)\cdot e^{-\gamma\rho_r^2}\right].\end{aligned} \tag{10}$$

In eq. (10) $\frac{\Delta i}{R\cdot T_{cr}} = I$.

Eq. 10 is transformed to

$$\begin{aligned}\left(\frac{\partial I}{\partial T_r}\right)_p &= z - 1 + T_r\cdot\left(\frac{\partial z}{\partial T_r}\right)_p + \rho_r\cdot\left(\frac{2b_3}{T_r^2} + \frac{6\cdot b_4}{T_r^3}\right) - \frac{3\cdot c_4}{T_r^3\cdot\gamma}\cdot\left[\beta + 1 - \left(\beta + 1 + \gamma\cdot\rho_r^2\right)\cdot e^{-\gamma\rho_r^2}\right] - \\ &- \left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot\left(b_2 + \frac{2b_3}{T_r} + \frac{3b_4}{T_r^2} + c_2\rho_r\frac{3\cdot c_3\cdot\rho_r^2}{T_r^3} - \frac{3c_3\rho_r}{T_r^2} - d_2\cdot\rho_r^4 + \frac{3c_4\rho_r}{T_r^2}\cdot e^{-\gamma\rho_r^2}\cdot\left(\beta + \gamma\cdot\rho_r^2\right)\right).\end{aligned} \tag{11}$$

The derivative $\left(\frac{\partial z}{\partial T_r}\right)_p$ is obtained from eq. (2):

$$\begin{aligned}\left(\frac{\partial z}{\partial T_r}\right)_p &= B\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p + 2C\cdot\rho_r\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p + 5\rho_r^4\cdot D\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p + 2\rho_r\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot\frac{c_4}{T_r^3}\cdot\left[\beta + \gamma\cdot\rho_r^2\right]\cdot e^{-\gamma\rho_r^2} - \\ &- \frac{3\cdot c_4}{T_r^4}\cdot\rho_r^2\cdot\left[\beta + \gamma\cdot\rho_r^2\right]\cdot e^{-\gamma\rho_r^2} + \frac{c_4}{T_r^3}\cdot\rho_r^2\cdot 2\cdot\rho_r\cdot\gamma\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p\cdot e^{-\gamma\rho_r^2} + \\ &+ \frac{c_4}{T_r^3}\cdot\rho_r^2\cdot\left[\beta + \gamma\cdot\rho_r^2\right]\cdot e^{-\gamma\rho_r^2}\cdot(-2\cdot\gamma\cdot\rho_r)\cdot\left(\frac{\partial \rho_r}{\partial T_r}\right)_p.\end{aligned} \tag{12}$$

Another equation for the derivative $\left(\frac{\partial z}{\partial T_r}\right)_p$ is obtained by differentiation of the $z = \frac{p_r}{T_r\cdot\rho_r}$ over T_r:

$$\left(\frac{\partial z}{\partial T_r}\right)_p = p_r \cdot \left[-\frac{1}{\rho_r \cdot T_r^2} - \frac{1}{\rho_r^2 \cdot T_r} \cdot \left(\frac{\partial \rho_r}{\partial T_r}\right)_p \right] = -\frac{p_r}{\rho_r \cdot T_r^2} \cdot \left[1 + \frac{T_r}{\rho_r} \cdot \left(\frac{\partial \rho_r}{\partial T_r}\right)_p \right] =$$
$$= -\frac{z}{T_r} \cdot \left[1 + \frac{T_r}{\rho_r} \cdot \left(\frac{\partial \rho_r}{\partial T_r}\right)_p \right] \tag{13}$$

Simultaneous solution of the eq. (12) and (13) gives

$$\left(\frac{\partial \rho_r}{\partial T_r}\right)_p = \frac{\Omega}{\Theta}, \tag{14}$$

where $\Omega = \frac{3 \cdot c_4}{T_r^4} \cdot \rho_r^2 \cdot \left[\beta + \gamma \cdot \rho_r^2\right] \cdot e^{-\gamma\rho_r^2} - \frac{z}{T_r}$;

$$\Theta = B + 2 \cdot C \cdot \rho_r + 5 \cdot D \cdot \rho_r^4 + \frac{z}{\rho_r} + \frac{2 \cdot c_4 \cdot \rho_r}{T_r^3} \cdot e^{-\gamma\rho_r^2} \cdot \left[\beta + \gamma \cdot \rho_r^2 + \gamma \cdot \rho_r^2 \cdot \left(1 - \beta - \gamma \cdot \rho_r^2\right)\right].$$

Then the derivative $\left(\frac{\partial z}{\partial T_r}\right)_p$ can be obtained from eq. (13). The specific heat at constant pressure correction is estimated from eq. (11).

4. COMPUTATION RESULTS

The computation of the gas mixture thermodynamic parameters was implemented by the Zagoruchenko method and the Lee-Kesler method for pressure range $p = 0{,}7 \div 20 MPa$ and temperature range $T = 250 \div 450 K$ for the various compositions. Some computation results are shown in Figures 1, 2 and 3 for the gas composition: methane – 0,9863; ethane – 0,0012; propane – 0,0023; N-butane – 0,0001; nitrogen – 0,0101 (in inclusion volume fractions).

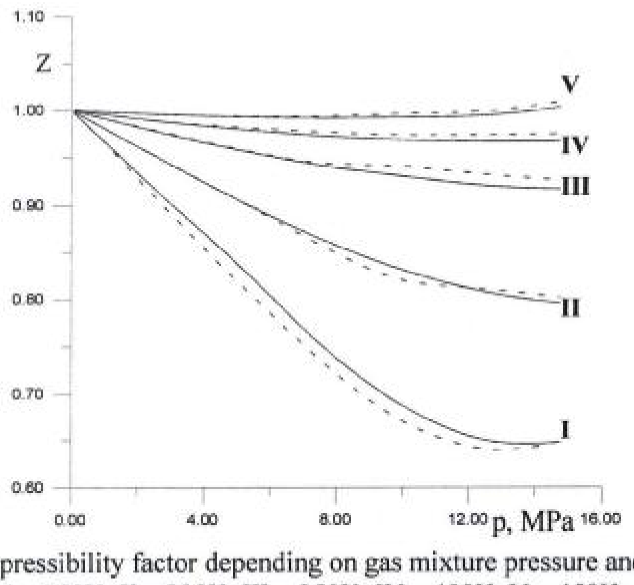

Figure 1. Compressibility factor depending on gas mixture pressure and temperature:
I – 250K; II – 290K; III – 350K; IV – 400K; V – 450K;
——— the Zagoruchenko method; - - - the Lee-Kesler method

The values of compressibility factor, calculated by these methods for designated pressure and temperature range (Figure 1), differ at most by 1%. At 290K and over the differences in values of compressibility factor are within (are not exceeding) 0,5 %. The differences in values of density are less (Figure 2), at 250K these are within 0,5%, at 290K and over – within 0,2 – 0,3 %.

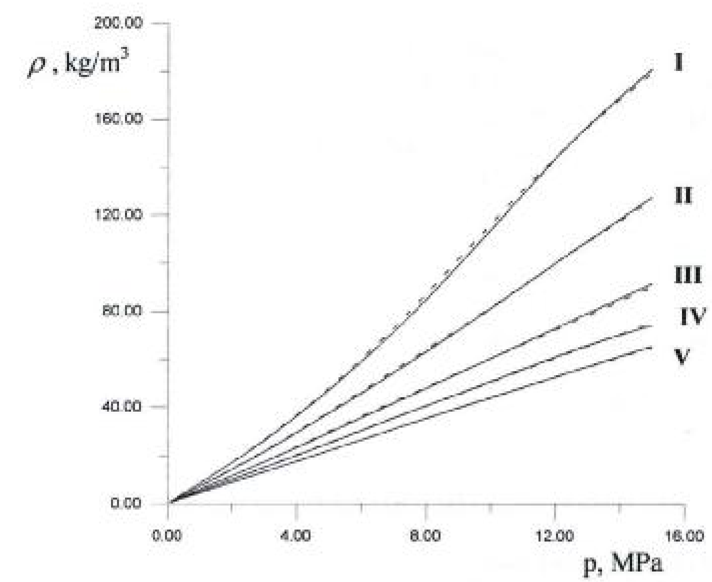

Figure 2. Density depending on gas mixture pressure and temperature:
I – 250K; II – 290K; III – 350K; IV – 400K; V – 450K;
—— the Zagoruchenko method; - - - the Lee-Kesler method

The values of specific heat at constant pressure, enthalpy and entropy differ more considerably, especially at range of low temperatures. At the same time the enthalpy differences, calculated for the pressure ratio Π=1,5 (Figure 3) by the Zagoruchenko method and the Lee-Kesler method differ within 1,5%.

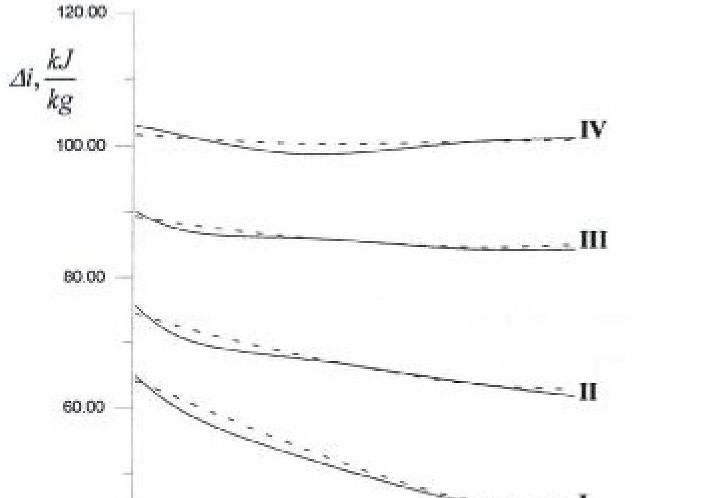

Figure 3. The enthalpy change depending on gas mixture pressure and temperature:
I – 250K; II – 290K; III – 350K; IV – 400K; V – 450K;
—— the Zagoruchenko method; - - - the Lee-Kesler method

5. CONCLUSIONS

The computer program for the computation of the thermodynamic properties of gas mixtures, solving the Benedict – Webb – Rubin state equation by means of the Lee-Kesler method was designed. Program was developed in the development environment Delphi using programming language Object Pascal. The advantage of this method as compared with others (for example, with the Zagoruchenko method) is providing the computation of the larger number of gas mixtures with different composition.

The analytical dependence for the estimation of the specific heat at constant pressure isothermal correction was obtained. The implemented computation showed that satisfactory accuracy of the thermal parameters estimation at the gas state zone away from phase transformation is provided. Also the satisfactory accuracy is provided for the enthalpy change estimation during gas mixture compression and expansion.

Not recommended to use this method for calculation of gas mixtures caloric parameters for the close to phase transformation zone.

6. REFERENCES

Reid R., Prausnitz J., Sherwood T. 1977, *The properties of gases and liquids*, New York, 592 p.

Zagoruchenko V., Bikchentay R., Vasserman A. et al. 1980, *Teplotehnicheskiye rascheti processov transporta i regazifikacii prirodnih gazov. Spavochnoe posobiye* [*Thermotechnical calculation of natural gas transport and gasification processes. Reference book* (In Russian).], Nedra, Moscow, 320 p.

NOMENCLATURE

A = estimated parameter;
ω = acentric factor;
z = compressibility factor;
i = specific enthalpy [kJ/kg];
s = specific entropy [kJ/(kg·K)];
c_p = specific heat at constant pressure [kJ/(kg·K)];
p = pressure [MPa];
ρ = density [kg/m^3];
T = temperature [K];
R = gas constant [kJ/(kg·K)];
$B, C, D, b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, \beta, \gamma$ = coefficients of the BWR equation of state, which depend on the gas composition.

Subscripts

bs = basic substance;
rs = reference substance;
id = ideal gas condition;
r = reduced state parameter;
i = initial gas condition;
f = final gas condition;
cr = critical gas parameter.