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THE EFFECT OF GEOS-TYPE TEMPERATURE FUNCTION ON THE THERMODYNAMIC PROPERTIES PREDICTION

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In this work we propose a modification of the temperature function of GEOS3C equation of state, in order to avoid the problem of the discontinuity of some thermodynamic properties at critical point. The suggested modification of the temperature function in the cohesion parameter of the GEOS3C equation solves the mentioned physical inconsistency. The GEOS3C equation of state, with the original and the proposed modification of temperature functions, is used to calculate the thermodynamic properties for ethane. The modified temperature function has the important advantage to not involve a reoptimization of C_1, C_2, C_3 parameters of GEOS3C equation, the available values in the literature being used to predict the thermodynamic properties of pure components with the modified temperature function.

Keywords: equation of state, thermodynamic properties, ethane

List of symbols

a, b, c, d	- parameters in GEOS
AAD	- absolute average deviation
B	- dimensionless parameter in GEOS3C, eq. (5)
C_1, C_2 and C_3	- parameters in GEOS3C temperature function
H	- enthalpy
M	- molar mass
P, P^S	- pressure, saturation pressure
R	- universal gas constant
S	- entropy
T	- temperature
V, V^L, V^V	- molar volume, liquid volume, vapor volume
Y	- thermodynamic function (general notation)

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Z	- compressibility factor

Greeks

α_c	- Riedel's criterium (parameter in GEOS)
β	- reduced temperature function in GEOS
Ω_a, Ω_b, Ω_c, Ω_d	- parameters of GEOS
ω	- acentric factor

Subscripts

c	- critical property
r	- reduced property

1. Introduction

In the classical thermodynamic framework it is possible to obtain typical relationships for the calculation of enthalpy, entropy, fugacity and other thermodynamic properties. These properties can be related to operating variables of the processes, e.g. the temperature of a fluid in a heat exchanger. It is therefore important to establish relationships between the properties and independent variables like temperature or pressure. Such relationships for thermodynamic properties of fluids can be obtained using equations of states [1].

Despite their known weaknesses, cubic equations of state of the van der Waals type continue to be used as important tools for chemical engineering applications.

In order to predict accurate values for a wide range of fluid thermodynamic properties, an equation of state must first be able to properly represent the thermodynamic behavior of pure substances.

A new form of the cubic general equation of state GEOS [2], named GEOS3C [3], was used in previous works for predicting the thermodynamic properties of many pure components and component mixtures [4-6]. The advantage of the model was determined by the introduction of a flexible function $\beta(T_r)$, in the cohesion parameter a of GEOS3C. As pointed out [3], the second derivative of the function $\beta(T_r)$ in GEOS3C is not continuous, and this fact leads to a discontinuity in the isochoric and isobaric heat capacities and other properties involving the second derivative, at the critical point.

In this work we propose a modification of the $\beta(T_r)$ in GEOS3C equation, in order to avoid the problem of the discontinuity of the thermodynamic properties at critical point. According to the example of ethane shown in this work, the suggested modification of the temperature function in the cohesion parameter of the GEOS3C equation solves the mentioned physical inconsistency. Moreover, it has the important advantage to not involve a reoptimization of C_1, C_2, C_3 parameters of GEOS3C equation, the available values in the literature being used to predict the thermodynamic properties of pure components with the modified temperature function.

2. The GEOS3C equation of state

The general cubic equation of state (GEOS) has the form [1]:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2+c} \tag{1}$$

The four parameters a, b, c, d for a pure component are expressed by:

$$a = a_c\,\beta(T_r); \quad a_c = \Omega_a \frac{R^2T_c^2}{P_c}; \quad b = \Omega_b \frac{RT_c}{P_c}; \tag{2}$$

$$c = \Omega_c \frac{R^2T_c^2}{P_c^2}; \quad d = \Omega_d \frac{RT_c}{P_c}; \tag{3}$$

The expressions of the parameters Ω_a, Ω_b, Ω_c, Ω_d are:

$$\Omega_a = (1-B)^3; \qquad \Omega_b = Z_c - B; \tag{4}$$

$$\Omega_c = (1-B)^2(B-0.25); \qquad \Omega_d = Z_c - 0.5(1-B) \tag{5}$$

$$B = \frac{1+C_1}{\alpha_c + C_1} \qquad \alpha_c \text{ - Riedel's criterion} \tag{6}$$

Riedel's criterion, α_c, is calculated using the acentric factor from the equation:

$$\alpha_c = 5.808 + 4.93\omega \tag{7}$$

The original temperature function for GEOS3C is:

$$\beta(T_r) = (1 + C_1 y + C_2 y^2 + C_3 y^3)^2 \qquad \text{for } T_r \le 1 \tag{8}$$

$$\beta(T_r) = (1 + C_1 y)^2 \qquad \text{for } T_r > 1 \tag{9}$$

$$y = 1 - T_r^{0.5} \tag{10}$$

The C_1, C_2 and C_3 parameters can be obtained by matching points on the saturation curve (vapour pressures together with the corresponding liquid volumes). A data base containing the parameters for 80 pure components is available in the literature [1].

The temperature function (8-10) as well as its first derivative are continuous in the critical point. The second derivative is not continuous, and this fact leads to a discontinuity in the isochoric and isobaric heat capacities and other properties involving the second derivative, at the critical point. This discontinuity is generally of the order of some J/mole/K and it seems that do not lead to difficulties in the calculations, near the critical point.

In order to avoid this discontinuity we suggest a modification of the temperature function, by extending its use to the entire T_r range:

$$\beta(T_r) = (1 + C_1 y + C_2 y^2 + C_3 y^3)^2 \quad \text{for } \forall\ T_r \tag{11}$$

The second derivative discontinuity has an effect on the isochoric and isobaric heat capacities as can be seen from the following equations [3, 5]:

$$\Delta C_V^R = \left[\frac{\partial(\Delta U^R)}{\partial T}\right]_V = T\frac{\partial^2 a}{\partial T^2}E \tag{12}$$

$$\Delta C_P^R = \Delta C_V^R - T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \tag{13}$$

with

$$E = \frac{1}{2\sqrt{-c}}\ln\frac{V-d+\sqrt{-c}}{V-d-\sqrt{-c}}\text{; for } c<0 \tag{14}$$

Moreover, the new temperature function (11) has the important advantage to not involve a reoptimization of C_1, C_2, C_3 parameters of GEOS3C equation, the available values in the literature [1] being used to predict the thermodynamic properties of pure components with the modified temperature function.

As discussed pertinently in a detailed analysis [7], the Soave-type cohesion function (2, 9) has pitfalls, leading to the prediction of multiple mechanically stable critical points and Joule-Thomson inversion curves for pure components. This anomalous behavior usually appears at very high temperatures [7], i.e. $T_r > 10$, and thus the results of this paper are not affected by such pitfalls, involving temperatures $T_r < 2$.

In this work, we illustrate several thermodynamic properties of ethane calculated with the GEOS3C modified function, eq. (11), in comparison with the original temperature function, eqs. (8-10).

3. Results and discussion

The GEOS3C equation of state, with the original (8-10) and the proposed modification (11) of temperature functions, was used in this work to calculate the phase equilibrium and the thermodynamic properties for ethane. The investigated *PVT* range covers single-phase (liquid or gas) and two-phase (liquid-vapor) regions, using recommended NIST data [8] as pseudo experimental values. The calculations were made with the software package PHEQ (Phase Equilibria) developed in our laboratory [9].

Table 1

Values of C_1, C_2, C_3, parameters for ethane. Critical data and acentric factor from NIST database [8]

Comp.	C_1	C_2	C_3	T_c (K)	P_c (bar)	Z_c	ω
Ethane	0.2163	0.3374	-0.0572	305.3	48.7	0.2793	0.0993

The values of the C_1, C_2, C_3 parameters of the GEOS3C equation, the critical data and acentric factor for ethane are presented in Table 1.

The following thermodynamic properties have been predicted: compressibility factor (Z), enthalpy (H), enthalpy of vaporization ($\Delta^v H$), entropy (S), isobaric heat capacity (C_P), isochoric heat capacity (C_V), heat capacity ratio (C_P/C_V), speed of sound (Ws), fugacity coefficient (φ), Joule-Thomson coefficient, (JT). No data on these thermodynamic properties were used for optimization of the C_1, C_2, C_3 parameters in this work. The ideal gas contribution to the thermophysical properties was calculated using the heat capacity function recommended in [9].

Table 2

Thermodynamic function deviations in single-phase region for ethane (isotherms). Temperature range (K): 100 – 625. Pressure range (bar): 1.0×10^{-3} – 700. Number of data points: 310

	AAD		AAD (%)				
EOS	***S*** kJ/kg/K	***H*** kJ/kg	***Z***	C_P	W_S	C_P/C_V	***JT***
GEOS3C (8-10)	0.06	11.1	2.4	4.6	23.6	2.2	27.2
GEOS3C (11)	0.06	10.7	2.7	4.5	24.0	2.6	28.5

Table 3

Thermodynamic function deviations in single-phase region for ethane (isobars and isochors). Temperature range (K): 100 – 625. Pressure range (bar): 1.0×10^{-3} – 700. Number of data points: 274 (isobars), 510 (isochors)

	AAD (%)						
	Isobars			Isochors			
EOS	*V*	*H*	*S*	*P*	*S*	*U*	*Cv*
GEOS3C(8-10)	3.4	30.6	2.9	3.6	1.2	1.3	3.3
GEOS3C(11)	3.9	30.4	2.8	4.7	1.8	1.9	3.5

Tables 2 and 3 show the deviations in several thermodynamic properties obtained with GEOS3C equation by using the two temperature functions presented above. The predictions of the properties at $T_r \leq 1$ are the same for both temperature functions, and are not reported in this work, being available in another paper [11].

The values of relative average absolute deviations (AAD %), and the average absolute deviations (AAD) are calculated by the equations:

$$\text{AAD (\%)} = \frac{\sum_{i=1}^{N} \left| (M_i^{eos} - M_i^{\exp}) / M_i^{\exp} \right| \cdot 100}{N} \tag{15}$$

$$\text{AAD} = \frac{\sum_{i=1}^{N} \left| M_i^{eos} - M_i^{\exp} \right|}{N} \tag{16}$$

where M is the corresponding thermodynamic property.

We can observe that no significant difference exist for the *PVT* and thermodynamic properties predicted by GEOS3C equation with the original (8-10) and the modified (11) temperature functions.

In the figures below we illustrate several thermodynamic properties predicted by GEOS3C with the two temperature functions, in the supercritical range for ethane.

Fig. 1 shows the pressure – density diagram for ethane. Points figure NIST data, while the curves are calculated with the GEOS3C with the two temperature functions, for four isotherms (critical and three supercritical isotherms).

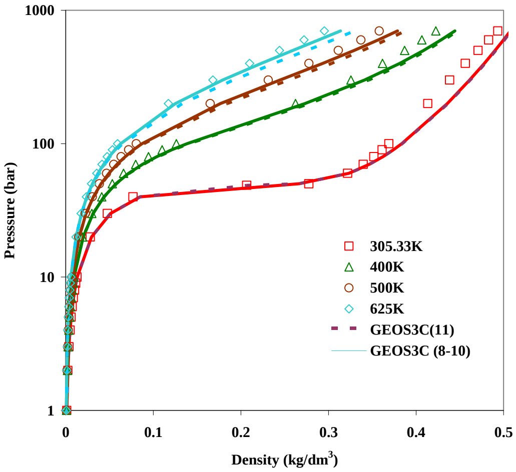

Fig. 1. Pressure – density diagram for ethane (critical and three supercritical isotherms) predicted with the two temperature functions of GEOS3C

As it can be seen, at the highest temperatures (500 K and 625 K) appears a difference between the predictions of densities with the temperature functions.

The calculation with the original temperature function is in better agreement with the NIST data.

In Fig. 2 is presented the pressure – isobaric heat capacity diagram for ethane (critical and three supercritical isotherms) predicted with the two temperature functions of GEOS3C. In this case, the results obtained with the new temperature function reproduce better the NIST data.

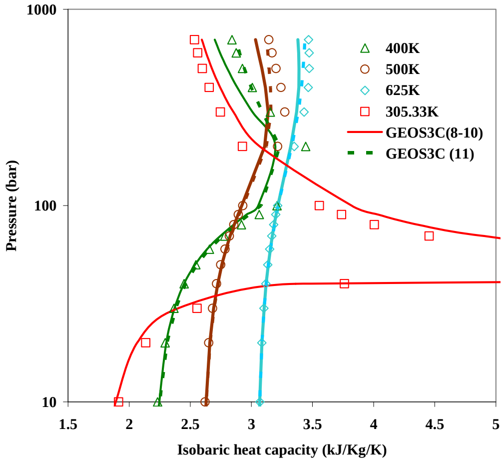

Fig. 2. Pressure – isobaric heat capacity diagram for ethane (critical and three supercritical isotherms) predicted with the two temperature functions of GEOS3C

In Figs. 3 and 4 we show the temperature – entropy diagrams predicted with the original and the modified temperature functions of GEOS3C.

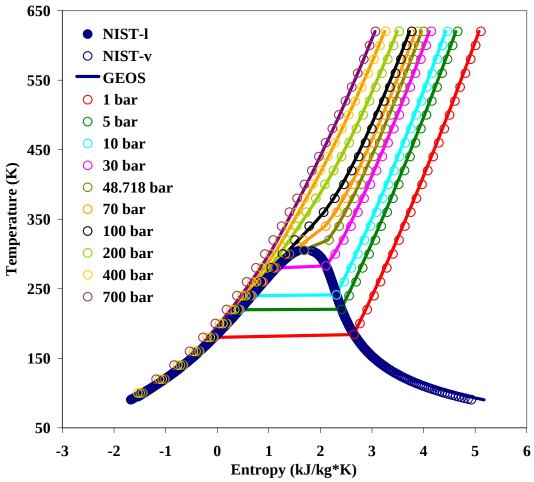

Fig. 3. Temperature – entropy diagram for ethane (isobars) predicted with GEOS3C (8-10)

At high pressures (400 and 700 bar), it appears a difference between the predictions obtained with the two temperature functions. The original temperature function leads to results in a slight better agreement with the NIST data.

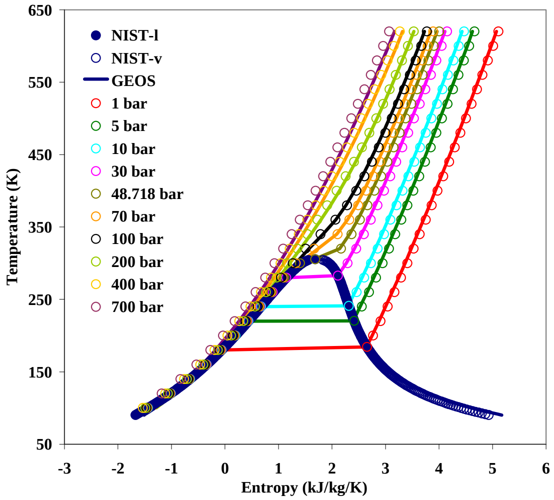

Fig. 4. Temperature – entropy diagram for ethane (isobars) predicted with GEOS3C (11)

In Fig. 5, the pressure – adiabatic coefficient prediction for supercritical isotherms with GEOS3C (8-10) and GEOS3C (11) is presented. At high temperatures, over 400 K, a difference between the temperature functions appears. The calculations with the original temperature function are in better agreement with the NIST data.

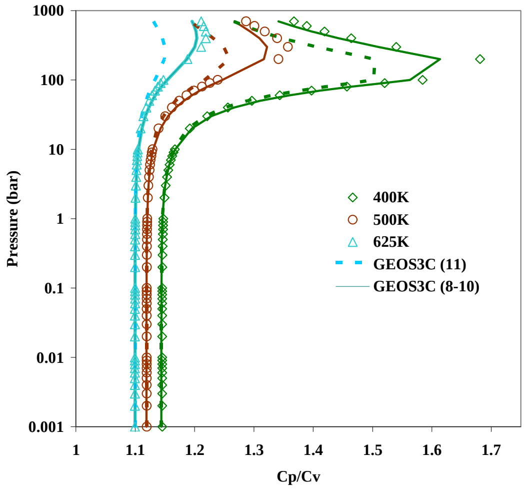

Fig. 5. Pressure – adiabatic coefficient diagram (supercritical isotherms) predicted with GEOS3C (8-10) and GEOS3C (11)

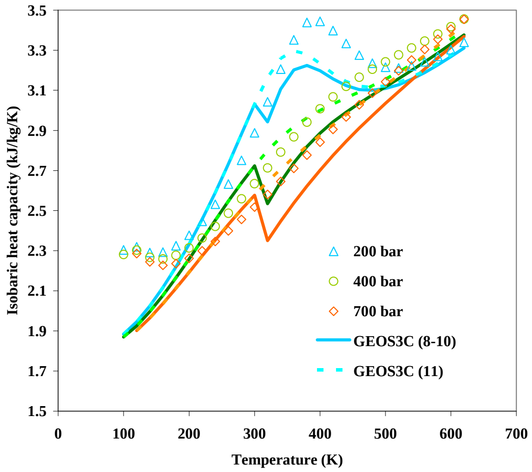

Fig. 6. Isobaric heat capacity – temperature diagram (supercritical isobars) predicted with GEOS3C (8-10) and GEOS3C (11)

Fig. 6 shows isobaric heat capacity – temperature diagram (supercritical isobars) for ethane, predicted with GEOS3C (8-10) and GEOS3C (11). The second derivative of the original temperature function, eqs. (8-10), is not continuous, and this fact leads to a discontinuity in the isobaric heat capacity (see the figure). The second derivative of the modified temperature function eq. (11) is continuous over the entire T_r range and as consequence the isobaric heat capacity is continuous. Supplementary, as can be seen in the fig. 6, this new function reproduces better the NIST isobaric heat capacity data for all supercritical isobars.

4. Conclusions

The second derivative of the function $\beta(T_r)$ in GEOS3C is not continuous, and this fact leads to a discontinuity in the isochoric and isobaric heat capacities and other properties involving the second derivative, at the critical point.

We propose a modification of the $\beta(T_r)$ in GEOS3C equation, in order to avoid the problem of the discontinuity of the thermodynamic properties at critical point.

According to the example of ethane shown in this work, the suggested modification of the temperature function in the cohesion parameter of the GEOS3C equation solves the mentioned physical inconsistency.

Moreover, it has the important advantage to not involve a reoptimization of C_1, C_2, C_3 parameters of GEOS3C equation, the available values in the literature being used to predict the thermodynamic properties of pure components with the modified temperature function.

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