Comparison of the Efficiency of Polynomial and Exponential Forms of Equation of State[1]

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ABSTRACT

The efficiency of two wide-spread forms of unified equation of state for gas and liquid was investigated. These forms are simple polynomial equation and equation with additional exponential terms of density. The last equation is similar to modified Benedict-Webb-Rubin equation. The calculations were fulfiled on the basis of data on thermodynamic properties of methane covering the temperature range from saturation line up to 620 K at pressures up to 1000 MPa.

The calculations showed that exponential equation ensures higher precision of approximation of used p,v,T - data than polynomial equation containing the same number of statistically most important coefficients. Root mean square deviations of calculated values of density from initial data for exponential equation are 1.2 - 1.8 times lower than for polynomial one (at number of coefficients from 30 to 45). However, both forms of equation are nearly equal concerning the satisfaction of Maxwell's rule and description of isochoric specific heat.

KEY WORDS: equation of state.

1. INTRODUCTION

At present many empirical equations of state for gas and liquid applicable over wide temperature and pressure ranges are compiled in the form

$$Z = 1 + b_1 \frac{\omega}{\tau^{0.5}} + \sum_{i=1}^{m} \sum_{j=0}^{s_i} b_{ij} \frac{\omega^i}{\tau^j} + \exp\left(-\gamma\omega^2\right) \sum_{i=1}^{n} \sum_{j=3}^{s_i} c_{ij} \frac{\omega^{2i}}{\tau^j} \quad , \qquad (1)$$

where $Z=pv/RT$ is the coefficient of compressibility, $\omega=\rho/\rho_{cr}$ is the reduced density, and $\tau=T/T_{cr}$ is the reduced temperature.

The peculiarity of the equation (1) - so-called modified Benedict-Webb-Rubin equation - is the presence of exponents of density. These exponents permit to describe p,v,T - data in a wide range of density with restricted number of terms of the equation . The initial BWR equation [1] was consecutive modified by several authors. The most effective form (1) was proposed by Jacobsen and Stewart [2]. Later on many scientists used this equation. In particular, recently Outcalt and McLinden [3] compiled equation of state (1) for some new refrigerants.

The investigators of former USSR used for analytic description of properties of fluids the polynomial equation of state

$$Z = 1 + \sum_{i=1}^{m} \sum_{j=0}^{s_i} b_{ij} \frac{\omega^i}{\tau^j} \quad . \qquad (2)$$

This equation may be interpreted as a part of virial equation of state, theoretically grounded for gases of low and moderate density. The application of equation (2) for dense gas and liquid is a convenient mathematical approach. The advantage of

this equation is its simplicity. Equation (2) was used by Soviet authors at preparing a series of monographs, for example [4].

Wagner and de Reuck [5] showed that equation of state in the form (2) for oxygen, compiled by Sychev and co-authors [4], describes p, v, T - data worse than exponential equation, compiled by Stewart and Jacobsen [6]. These equations contain practically the same numbers of coefficients, but they were compiled on the basis of different sets of experimental data with use of different weights of data. Therefore, we decided to compare the accuracy of approximation of the same massif of data by means of equations (1) and (2).

2. CALCULATIONS

The calculations were fulfiled on the basis of data on thermodynamic properties of methane. These data were obtained by means of fundamental equation of state compiled by Setzmann and Wagner [7], that describes experimental data with high precision. The mentioned equation containes both polynomial parts and exponential terms with power of density from one to four.

We used 533 values of density in the single-phase region on 24 isobars in pressure range 0.5 - 1000 MPa and temperature range 94 - 620 K. Fifty values of density of saturated vapor and liquid, covering the temperature range from the triple point (90.694 K) to 186 K were used also. On the melting line 18 values of density of liquid were taken at temperatures from 92 K to 254.8 K (up to reduced density ρ/ρ_{cr} =3.57). Accuracy of description of caloric properties was checked by 339 values of isochoric specific heat in the single-phase region up to 1000 MPa and 620 K and 50 values of c_v on the saturation line at temperatures 90.694 - 186 K.

The step of used data in the single-phase region and on the melting line increased with increase of pressure and temperature.

Equations of state (1) and (2) were compiled by means of specific version of stepwise regression method, developed by Wagner [8] and extended by de Reuck and Armstrong [9]. This method is based on selection of the statistically most important terms from empirical bank of terms of equation. Bank of terms for equation (2) contained 80 terms with powers of ω from 1 to 10 and powers of τ from 0 to 7. The bank for equation (1) contained additionally in the exponential part 60 terms with powers of ω from 1 to 12 and powers of τ from 1 to 5. Therefore, the exponential part of composed equations may contain more terms than MBWR - equation. It should be noted, that we do not include the term containing $\tau^{0.5}$ for unification of polynomial parts of equations (1) and (2).

At compiling both equations of state the unified set of weights was used. The values of weights were calculated by equation

$$w = \frac{1}{\left(\frac{Z}{\rho} + \frac{\partial Z}{\partial \rho}\right)^2 \left(\frac{\rho \delta \rho}{2}\right)^2} \quad , \qquad (3)$$

where the derivative $\partial Z/\partial \rho$ was calculated by means of equation of state [7]. The value of the relative error $\delta\rho$ was taken 0.05%.

The calculation of weights according to the formula (3) is based on assumption that the uncertainties of temperature and pressure are equal zero. This assumption is correct in our case. At using weights determined by (3) the deviations of calculated values of density from initial data are nearly equal in different regions of parameters.

On the basis of p, v, T - data [7] the first series of equations (1) and (2) with different number of coeffitients (from 30 to 45) was compiled. At compiling these equations the Maxwell's rule was satisfied by using the above-mentioned p, v, T - data for the saturation line on 25 isotherms.

In the second series of calculations we added the random errors to the values of density, calculated by equation of state [7]. These errors were distributed according to the normal law in the range from –0.05% to +0.05%. By means of transformed p, v, T - data we simulated the compiling equation of state on the basis of experimental data. On the basis of these data we compiled new equations of state in two discussed forms with the same numbers of coefficients. It should be stressed, that the equations with number of terms more than 34 were obtained by selection of lower values of significance of individual terms and of the equation as a whole.

3. RESULTS

By means of compiled equations of state the relative deviations $\delta\rho$ of calculated values of density from smooth or transformed data used at compiling the equations were determined. The deviations δp_s of values of saturated vapor pressure calculated on the basis of Maxwell's rule from data [7] were determined also. For the first series of equations the deviations δc_v of calculated values of isochoric specific heat from data [7] were determined. For the second series the deviations δc_v were calculated using values of c_v [7] with added random errors from –0.5% to +0.5%. At calculations of c_v the equation for isobaric specific heat c_{p0} of ideal gas presented in [7] was used.

Fig. 1 shows root mean square deviations $\delta\rho_m$ of calculated values of density from initial data as a function of the number of coefficients. As it is clear from this Figure, exponential equation in all cases ensures higher precision of approximation of p,v,T - data than polynomial equation with the same number of terms. Corresponding values of $\delta\rho_m$ for exponential equation are 1.4 - 1.8 times lower for the first series of equations and 1.2 - 1.4 times lower for the second series.

Plot of root mean square deviations δp_{sm} of calculated values of saturated vapor pressure from data [7] is shown in Fig 2. This plot in contrast to previous one is characterized by the scatter of results and does not testify advantages of exponential equation. In some cases the deviations δp_{sm} for polynomial equation are lower than for exponential one, especially at calculations on the basis of transformed data.

Plot of root mean square deviations δc_{vm} of calculated values of c_v from initial data is shown in Fig. 3. At calculations of these deviations 8 points on isotherm 94 K and 2 points for saturated liquid at temperatures 94 K and 90.694 K were excluded. For overwhelming majority of equations corresponding deviations were 10 - 30 % at 94 K and 30 - 50 % at the triple point. The use of these points at calculation of δc_{vm} may distort this value and hamper the comparison of two forms of equation.

It is interesting to note that the precision of satisfaction of Maxwell's rule at above-mentioned temperatures was ±(0.03 - 0.08)%. In two cases for exponential equation when deviations from Maxwell's rule were lower (0.003 - 0.009%), the corresponding values of δc_v were significantly lower also (near 3% at

94 K and near 5% at the triple point). This testifies the necessity of very high precision of satisfaction of Maxwell's rule near the triple point (by increasing the weights of corresponding data). The most reliable way is to use the data on isochoric specific heat of liquid at compiling the equation of state.

Fig. 3 shows that two forms of equation of state describe the data on isochoric specific heat with practically equal accuracy.

4. CONCLUSIONS

A comparison of precision of analytic description of data on thermodynamic properties of methane in a wide region of parameters by means of polynomial and exponential equations of state was fulfiled. The comparison showed that the latter equation with power of density in exponent equal 2 ensures higher precision of approximation of p,v,T - data. Nevertheless, both forms of equation ensure practically the same precision of satisfaction of Maxwell's rule and of description of data on isochoric specific heat.

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FIGURE CAPTIONS

Fig.1. Root mean square deviations dr_m of calculated values of density from initial data as a function of number of coefficients of equations (1) and (2):

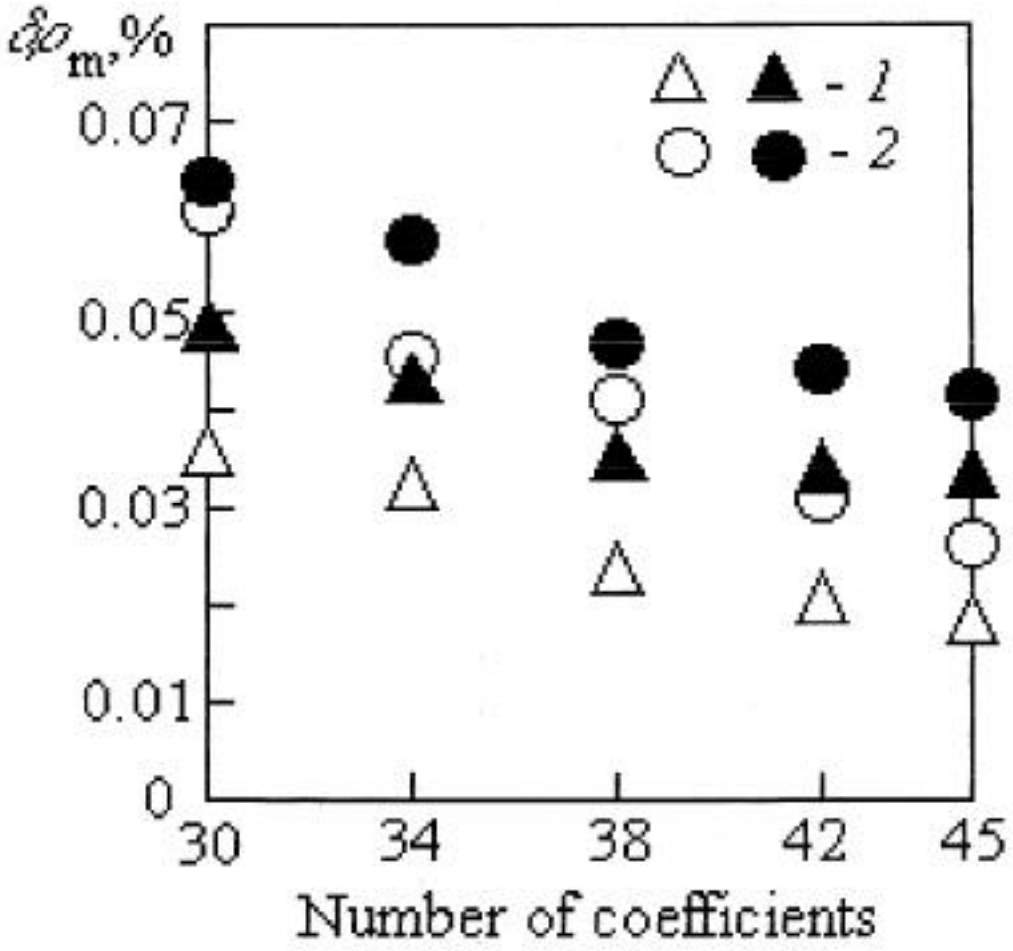
1 - for equation (1), 2 - for equation (2), light signs - for the first series of calculations, dark signs - for the second.

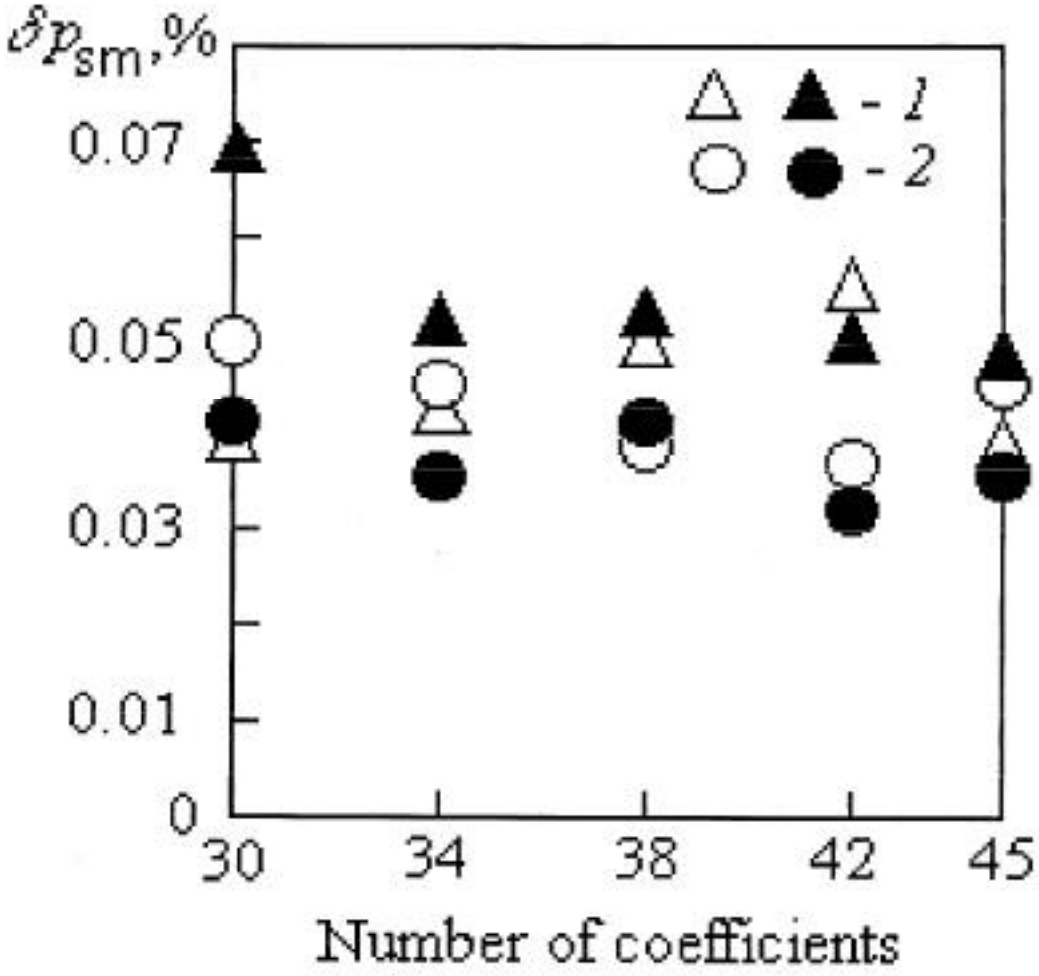
Fig.2. Root mean square deviations dp_{sm} of calculated values of saturated vapor pressure from data [7] as a function of number of coefficients of equations (1) and (2):

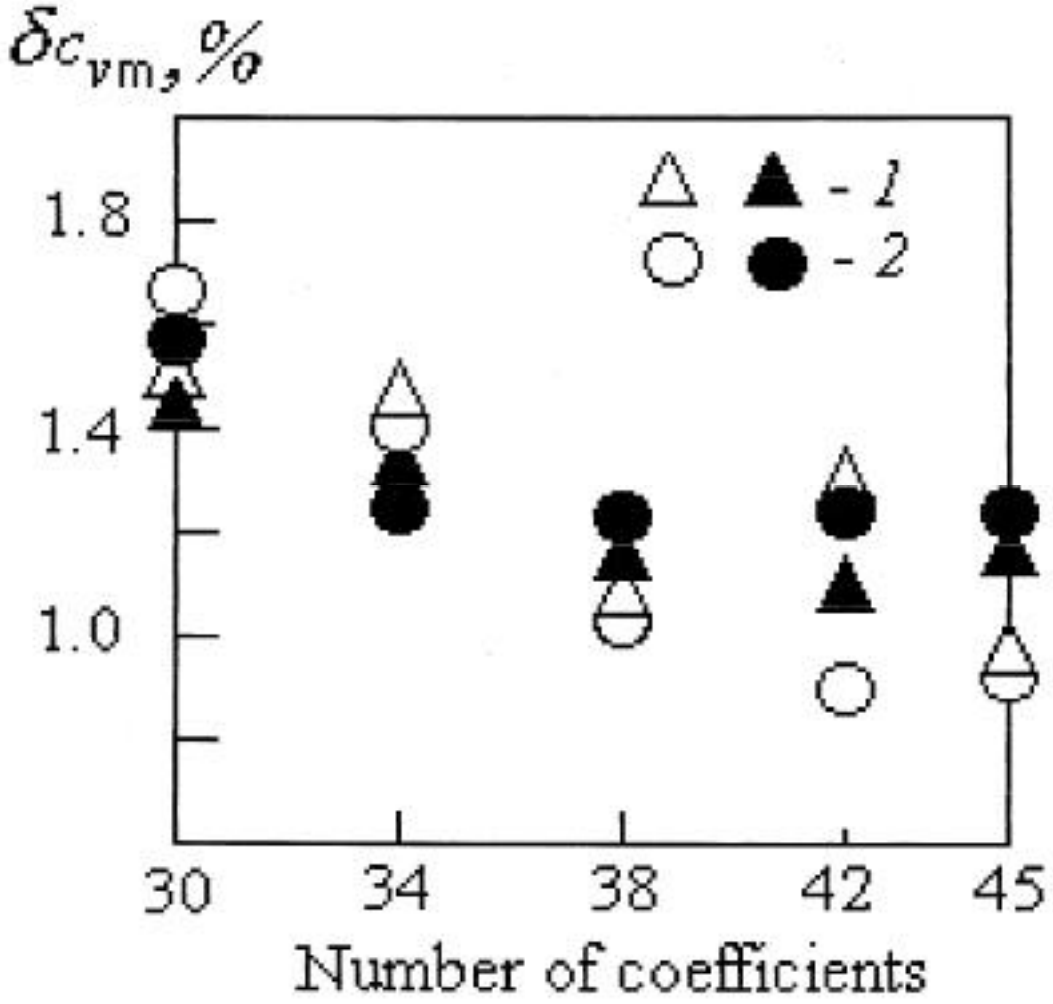
1 - for equation (1), 2 - for equation (2), light signs - for the first series of calculations, dark signs - for the second.

Fig.3. Root mean square deviations dc_{vm} of calculated values of isochoric specific heat from initial data as a function of number of coefficients of equations (1) and (2):

1 - for equation (1), 2 - for equation (2), light signs - for the first series of calculations, dark signs - for the second.


δo_m,%
0.07
0.05
0.03
0.01
0
30
34
38
42
45
Number of coefficients
- 1
- 2


δp_{sm},%
0.07
0.05
0.03
0.01
0
30
34
38
42
45
Number of coefficients
- 1
- 2


δc_{vm}, %
1.8
1.4
1.0
- 1
- 2
30
34
38
42
45
Number of coefficients