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A Simple Equation Of State For Calculating The Compressibility Factor Of Pure Fluids Based On The Virial EOS

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ABSTRACT

In this study a new simple equation based on the virial equation has been developed to predict the compressibility factor of nonpolar pure fluids. This equation is a third order polynomial and takes into account reduced pressure, reduced temperature and the second virial coefficient. The result from this equation have been compared with experimental data, Lee-Kesler and two term virial equations. This comparison shows good agreement between the equation and the experimental data. This equation also predicts the critical compressibility factor very good. After validating the equation, other thermodynamic properties such as enthalpy and entropy have been calculated and the results have been compared with experimental data.

KEYWORDS

Compressibility factor;
EOS;
Virial;
Enthalpy;
Entropy.

INTRODUCTION

From the viewpoint of engineering, the calculation of compressibility factor of pure fluids is important. Because in many industrial processes, the compressibility factor is needed for estimating of thermodynamics properties. Several attempts were made in the past for this purpose. The results of these attempts have been expressed in the form of an equation of state. These equations of state are virial equation, analytical EOS and nonanalytic EOS. The virial equation, which can be derived from molecular theory, but is limited in this range of applicability. Analytical EOS[1,2] which are cubic or quadratic in volume, therefore whose volumes can be found analytically from specified P and T. These equations can represent both liquid and vapor behavior over limited ranges of temperature and pressure for many but not all substance. Nonanalytic equations are applicable over much broader ranges of P and T than are the analytic equations, but they usually require many parameters that require fitting to large amounts of data of several properties. These models include empirical forms of original and modified Benedict-Webb-Rubin[3,4] as well as wagner models[4,5,6] , semi theoretical models such as perturbation models[7] that include higher order polynomials in density, chemical theory equations[8] for strongly associating species.

When selecting an EOS for PVT properties, users, should first evaluate what errors they will accept for the substance and conditions of interest, as well as the effort it would take to obtain parameter values if they are not available in the literature. Sometimes this takes as much effort as implementing a more complex, but accurate model such as a nonanalytic form. In this study a new simple equation of state with theoretical basis has been proposed. This EOS has been developed based on virial EOS to predict the compressibility factor, enthalpy and entropy of nonpolar pure fluids. The experimental data have been used to test the equation.

THEORY

The virial EOS was originally introduced by Kamerlingh Onnes as a series of ascending power of density to represent the compressibility factor Z. Later on, Ursell and Mayer[10] developed the statistical mechanical basis for the virial equation, which is formally presented as a series expansion of either the radial distribution function or the grand canonical partition function for low-density gases. The virial coefficients are related to the intermolecular potential energy so that B is related to the energy of interaction between pairs of molecules; C is related to the energy of interaction between triplets of molecules, and so forth.

The Leiden virial equation of state gives the compressibility factor as a power series in the reciprocal molar volume 1/V:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \quad (1)$$

The mathematically analogous power series in the pressure can be derived from equation (1) and is known as the Berlin virial EOS:

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots \quad (2)$$

Which, in above equation, the parameters B′, C′, D′, etc, and B, C, D, etc, are virial coefficients. The two sets of coefficients in Eqs(1) and (2) are related as follows:

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \quad B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{(RT)^2} \quad (3)$$

It was shown that Berlin virial EOS was superior to the Leiden virial EOS for calculating compressibility factor at high temperature for the Lennard-Jones gas and the real gases of methane, carbon dioxide and steam[16]. When Berlin virial EOS is truncated to four terms, the appropriate form of the equation(2) is:

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 \quad (4)$$

Substituting B′, C′, and D′ from equation(3) into equation (4) gives:

$$Z = 1 + \frac{BP}{RT} + \frac{(C - B^2)P^2}{(RT)^2} + \frac{(D - 3BC + 2B^3)P^3}{(RT)^3} \quad (5)$$

Equation(5) becomes:

$$Z = 1 + \frac{BP}{RT} + \frac{CP^2}{(RT)^2} - \frac{B^2P^2}{(RT)^2} + \frac{DP^3}{(RT)^3} - \frac{3BCP^3}{(RT)^3} + \frac{2B^3P^3}{(RT)^3} \quad (6)$$

In the above equation, values C and D like those of B depend on the gas and on temperature. However, much less is known about third and fourth virial coefficient than about second virial coefficients, though data for a number of gases are found in the literature[11]. For this reason, in equation(6), when the terms containing C and D are ignored, it is reduced to:

$$Z = 1 + \frac{BP}{RT} - \frac{B^2P^2}{(RT)^2} + \frac{2B^3P^3}{(RT)^3} \quad (7)$$

The equation (7) may be written as:

$$Z = 1 + \left(\frac{BP_C}{RT_C}\right)\frac{P_r}{T_r} - \left(\frac{BP_C}{RT_C}\right)^2\left(\frac{P_r}{T_r}\right)^2 + 2\left(\frac{BP_C}{RT_C}\right)^3\left(\frac{P_r}{T_r}\right)^3 \quad (8)$$

Pitzer and curl[12] proposed a correlation, which expresses the quantity $BP_c/R\,T_c$ as

$$\frac{BP_C}{RT_C} = f^{(0)}\left(\frac{T}{T_C}\right) + \omega f^{(1)}\left(\frac{T}{T_C}\right) \quad (9)$$

The function $f^{(0)}$ gives the reduced second virial coefficients for simple fluids(w=0) while $f^{(1)}$ is a correction function which, when multiplied by ω, gives the effect of acentricity on the second virial coefficient. The two function $f^{(0)}$ and $f^{(1)}$ were determined from experimental data for a number of nonpolar or slightly polar substances. As modified by tsonopoulos[13], these functions are

$$f^{(0)}\left(\frac{T}{T_C}\right)=0.1445-\frac{0.330}{T_r}-\frac{0.1385}{T_r^{\,2}}-\frac{0.0121}{T_r^{\,3}}-\frac{0.000607}{T_r^{\,8}} \qquad (10)$$

$$f^{(1)}\left(\frac{T}{T_C}\right)=0.0637+\frac{0.331}{T_r^{\,2}}-\frac{0.423}{T_r^{\,3}}-\frac{0.008}{T_r^{\,8}} \qquad (11)$$

Equation (8) may be written

$$Z=1+M-M^2+2M^3 \qquad (12)$$

Where

$$M=\left(\frac{BP_C}{RT_C}\right)\frac{P_r}{T_r} \qquad (13)$$

Equation (12) is modified as follows:

$$Z=1+aM+bM^2-cM^3 \qquad (14)$$

By using regression analysis of experimental data[14] for argon, carbon dioxide, krypton, nitrogen and oxygen, the values of a, b, and c are calculated as follows:

$$c=0.8\left(T_r^7/P_r\right)\quad b=0.94T_y^{5.3}/P_y\quad \alpha=1.65 \qquad (15)$$

It is mentioned that the compressibility factor at critical point is also calculated by equation(14). For calculating critical compressibility factor, the calculated compressibility factor at T_c and P_c by equation(14) must be divided by 2.

The enthalpy(H) and entropy(S) can be calculated from Z(Eq.14) as follows[18]

$$\frac{H^R}{RT_C}=-T_r^2\int_0^{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r} \qquad (16)$$

$$\frac{S^R}{R}=\int_0^{P_r}\left[1-Z-T_r\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\right]\frac{dP_r}{P_r} \qquad (17)$$

RESULTS

The compressibility factor of argon, air, carbon dioxide, krypton, methane, carbon monoxide, nitrogen, oxygen, and xenon at different temperature and pressure were predicted by equation(14) and the calculated values were compared with the experimental data[15] in figures 1 through 9. It can be seen that there is good agreement between the results of this equation and experimental data. Also, the results from equation(14) have been compared with Lee-Kesler and two terms virial equations in these figures. Although equation(14) has been developed for nonpolar fluids, it can be used for slightly polar fluids. In figure 6, experimental data and calculated results for carbon monoxide as a slightly polar fluid are compared. As can be seen in this figure, the results from the equation(14) are in good agreement with the experimental data. The average absolute percent deviation, AAPD for each fluid, is calculated by the following equation:

$$AAPD=\frac{1}{N}\sum_{i=1}^{N}\left|\left(\frac{Z_{exp}-Z_{cal}}{Z_{exp}}\right)_i\right|\times 100 \qquad (18)$$

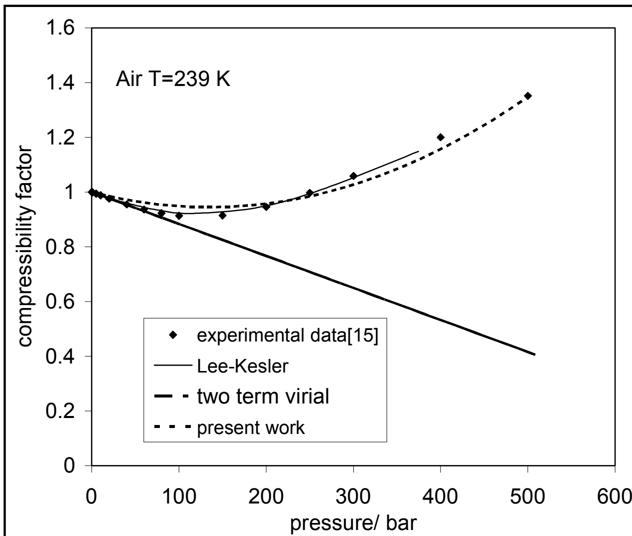

Figure 1: Compressibility factor versus pressure for air

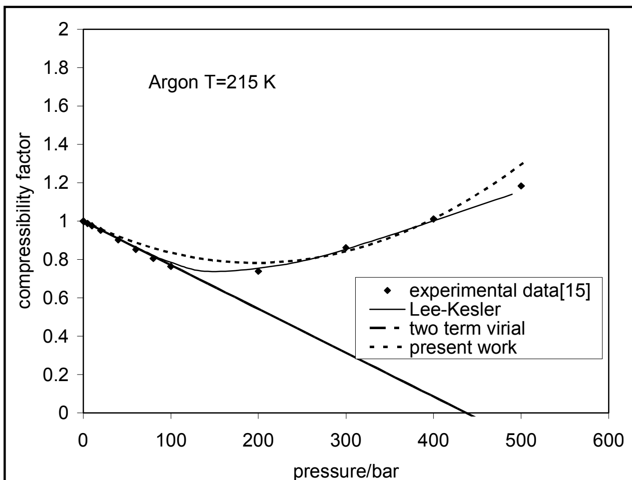

Figure 2: Compressibility factor versus pressure for argon

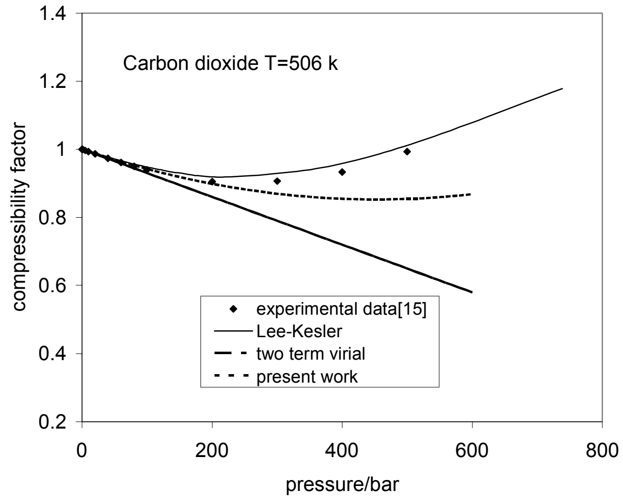

Figure 3: Compressibility factor versus pressure for carbon dioxide

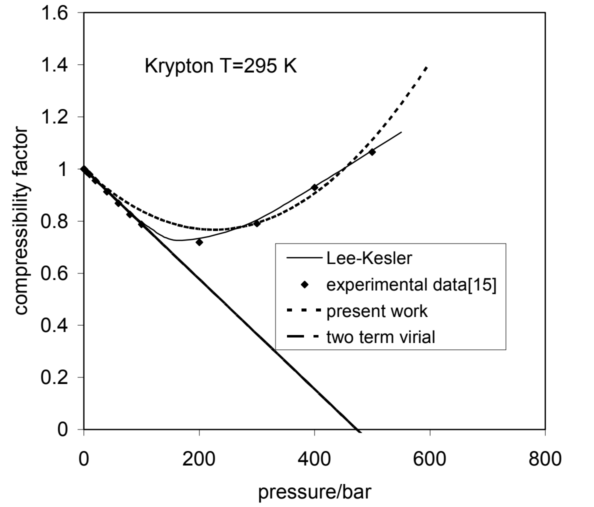

Figure 4: Compressibility factor versus pressure for krypton

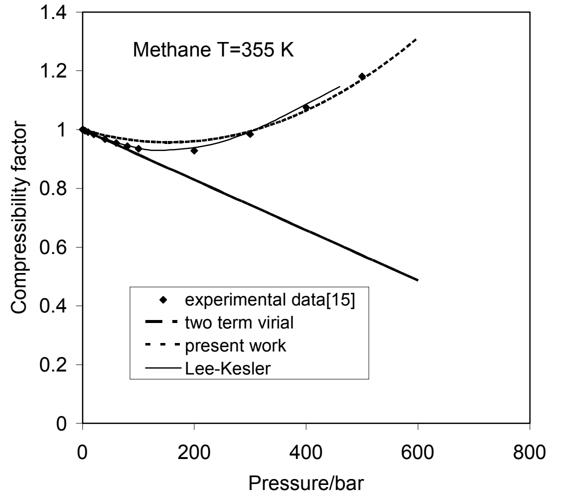

Figure 5: Compressibility factor versus pressure for methane

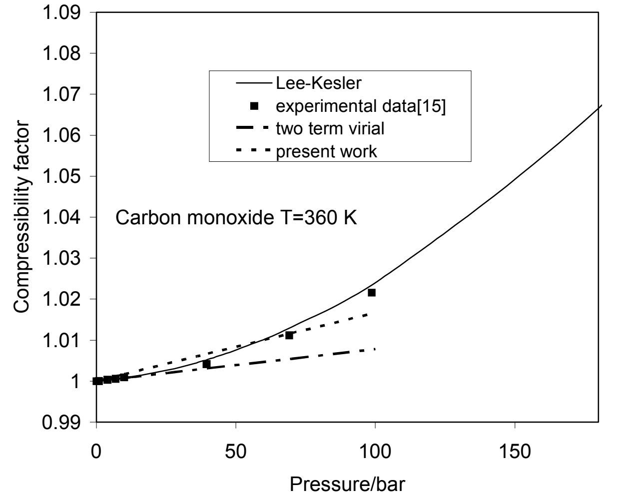

Figure 6: Compressibility factor versus pressure for carbon monoxide

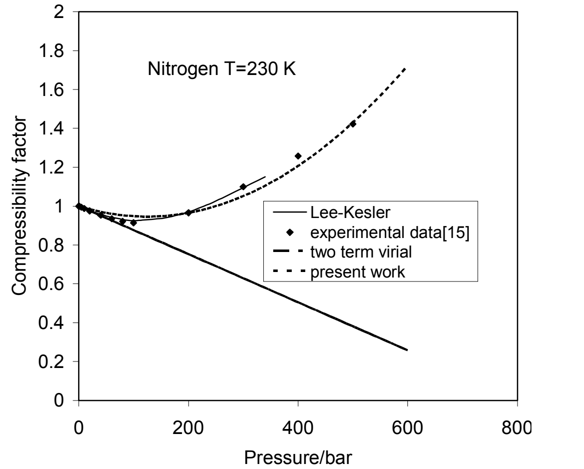

Figure 7: Compressibility factor versus pressure for nitrogen

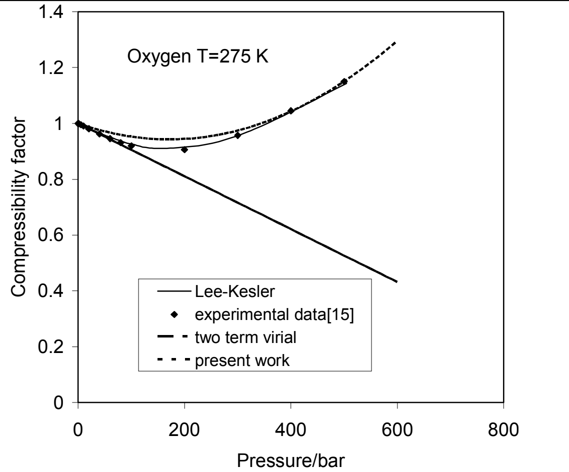

Figure 8: Compressibility factor versus pressure for oxygen

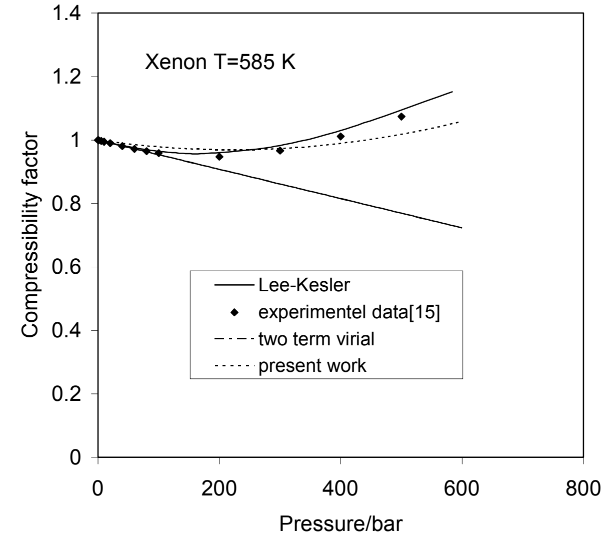

Figure 9: Compressibility factor versus pressure for xenon

In the above equation, N is the number of data point tested and the subscript exp. and cal. represent experimental and calculated values, respectively. The lowest values of AAPD for argon, air, carbon dioxide, krypton, methane, carbon monoxide, nitrogen, oxygen, and xenon have been calculated 3.44, 1.87, 2.36, 2.52, 1.35, 0.136, 1.88, 1.48, and 1.44 respectively. TABLE 1 presents the minimum and maximum of AAPD in compressibility factor prediction for mentioned fluids using equation(14). The critical compressibility factors of some pure fluids were predicted by equation(14) and the calculated values were compared with the experimental data[15]. The results of this comparison are presented in TABLE 2. As can be seen, the agreement between the predicted results and experimental data is excellent. In the next step the enthalpy of some pure fluids at different temperature and 1 atm were calculated by equation(16) and the results were compared with the experimental data[15] in figures 10 through 18. As can be seen in these figures, there is a very good agreement between the results and experimental data. TABLE 3 shows the average absolute percent deviation of predicted entropy using the equation(17) for some pure fluids. Small values of AAPD in this table indicate the good accuracy of the equation(14) for calculating of pure fluids entropy.

TABLE 1: Maximum and minimum AAPD in prediction of compressibility factor for some pure fluids by equation (14)

Fluid	Temperature range (K)	Pressure range (bar)	Min. of AAPD	Max. of AAPD
Krypton	260 - 710	0 – 600	2.52	10.80
Xenon	360 - 980	0 – 600	1.44	9.97
Methane	240 – 640	0 - 500	1.35	9.64
Nitrogen	160 – 425	0 - 500	1.88	9.88
Air	170 – 440	0 - 500	1.87	10.35
Oxygen	195 – 520	0 - 500	1.48	9.77
Carbon dioxide	350 - 950	0 - 500	2.36	9.62
Carbon monoxide	220 – 475	0 - 100	0.136	9.84
Argon	190 - 515	0 - 500	3.44	10.89

TABLE 2: Comparison between the experimental data[15] and calculated values for some pure fluids in predicting critical compressibility factor

Fluid	Z_c(calculated value)	Z_c(experimental value)	AAPD
Krypton	0.291	0.288	1.04
Xenon	0.291	0.286	1.70
Methane	0.290	0.289	1.39
Nitrogen	0.290	0.289	0.346
Air	0.290	0.289	0.346
Oxygen	0.290	0.288	0.690
Carbon dioxide	0.287	0.274	4.70
Carbon monoxide	0.290	0.299	3.00
Neon	0.291	0.292	0.342
Argon	0.291	0.291	0.00

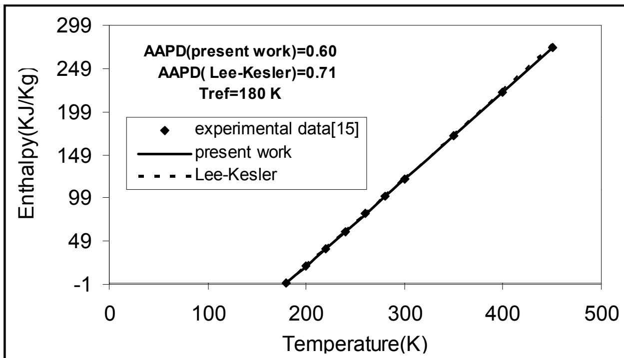

Figure 10: Enthalpy versus temperature for air at 1 atm

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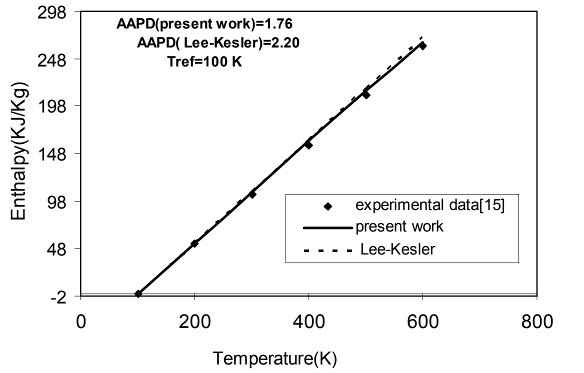

Figure 11: Enthalpy versus temperature for argon at 1 atm

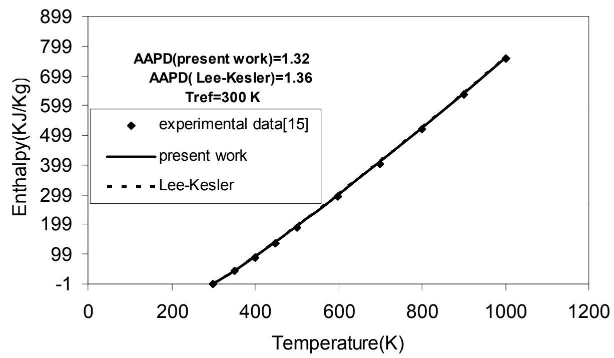

Figure 12: Enthalpy versus temperature for carbon dioxide at 1 atm

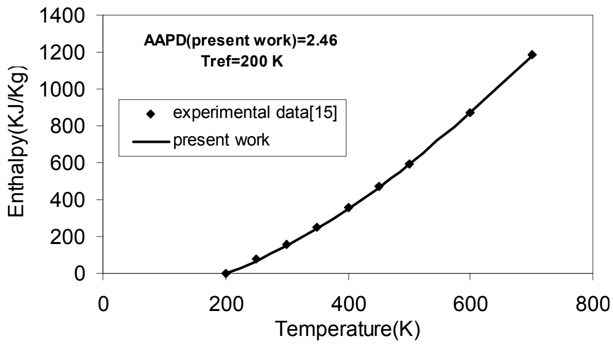

Figure 13: Enthalpy versus temperature for ethane at 1 atm

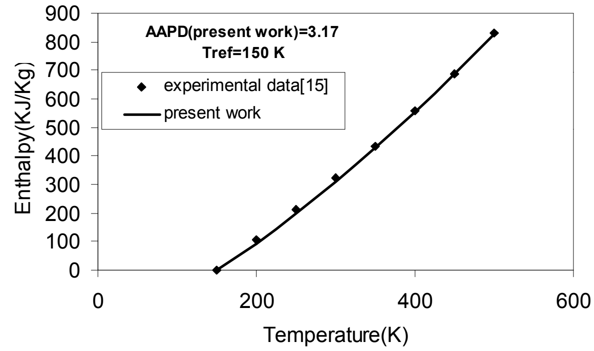

Figure 15: Enthalpy versus temperature for methane at 1 atm

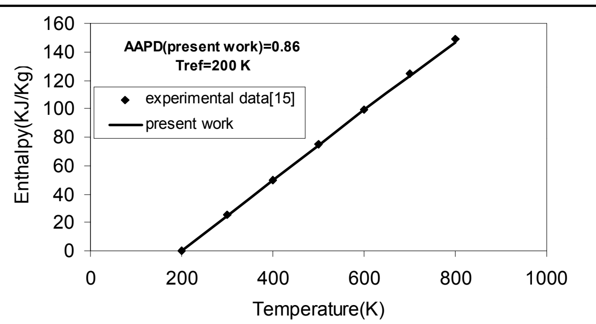

Figure 14: Enthalpy versus temperature for kyrpton at 1 atm

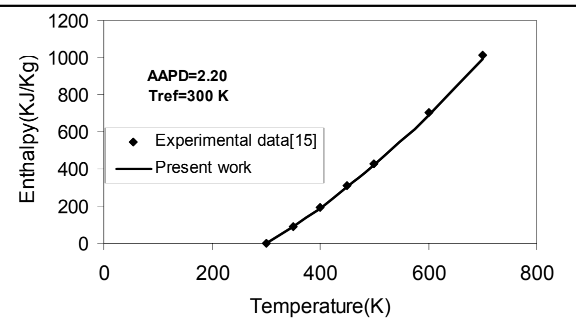

Figure 16: Enthalpy versus temperature for normal butane at 1 atm

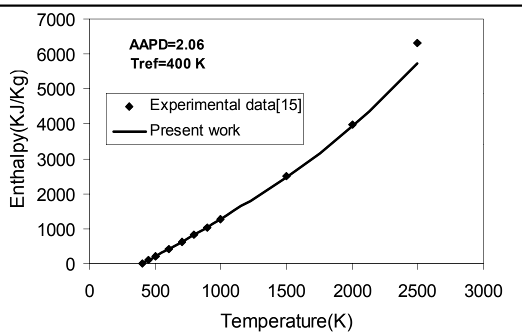

Figure 17: Enthalpy versus temperature for steam at 1 atm

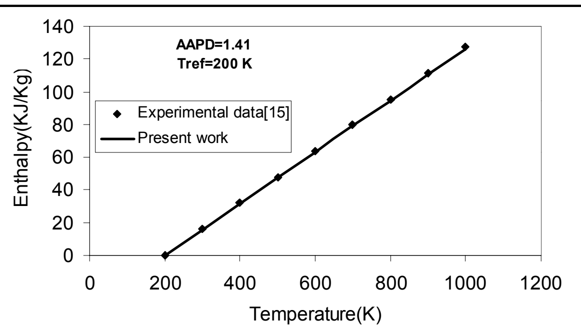

Figure 18: Enthalpy versus temperature for xenon at 1 atm

TABLE 3: AAPD in prediction of entropy for some pure fluids by equation(17)

Fluid	Temperature range(K)	AAPD
Air	180-450	0.5003
Argon	100-600	1.7582
Carbon Dioxide	300-1000	1.4315
Ethane	200-700	2.4242
Krypton	200-800	0.8655
Methane	150-500	3.7053
n-Butane	300-700	1.7130
Steam	400-2500	1.3114
Xenon	200-1000	1.5023

CONCLUSIONS

A new simple equation of state based on the virial equation proposed for calculating thermodynamic properties of nonpolar pure fluids. The current EOS, while good, is not quite as accurate complicated EOS. The prediction of enthalpy, entropy and critical compressibility factors of nonpolar pure fluids also represents very good performance of the new EOS. Our future work will extend this new simple equation to polar pure fluids and mixtures.

List of symbols

AAPD Average absolute percent deviation
a Coefficient in equation(14)
B, B′ Second virial coefficient
b Coefficient in equation(14)
C,C′ Third virial coefficient
c Coefficient in equation(14)
D,D′ Fourth virial coefficient
M Variable in equation(14)
N Number of data point
P Pressure
R Universal gas constant
T Temperature
V Molar volume
Z Compressibility factor Subscripts
c Critical values
calc Calculated
exp Experimental
r Reduced values Greek letters
ω Acentric factor

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