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Theoretical study of third virial coefficient with Kihara potential

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Abstract: In this paper, a new formula has been presented for accurate calculation of the third virial coefficient with Kihara potential. The obtained formula allows us to the determination of thermodynamic properties of imperfect gases. The validity of the formula has been tested by application to some gases C_2H_6 , C_3H_8 , $C(CH_3)_4$ and $n-C_5H_{12}$. The obtained results have been compared with the other studies. These comparisons show that the formula developed in this study are in good agreement with the data available in the literature.

Keywords: Virial coefficient; Third virial coefficient; Kihara potential

1. Introduction

The determination of the equations of state are an important issue to define thermodynamic properties (heat capacity, internal energy, sound velocity, etc.) of imperfect gases [1-3]. Many equations of state have been proposed to accurate evaluation of the thermodynamic properties of imperfect gases [3, 4]. One of equation of state is the virial equation of state. The importance of the virial equation of state lies in its direct relation to intermolecular interaction [5,6]. The Lennard-Jones ($2n-n$) potential that it is described the interaction between simple spherical molecules only, has been extensively studied by both experimental and theoretical methods [7]. Kihara potential is defined the interaction between two more complex molecules and found wide applications because of its well definition of thermodynamic properties [7, 8]. In spite of many studies, the evaluations of the third virial coefficient for various types of the intermolecular interaction are still one of the main crucial problems in physics and biophysical chemistry [9-11].

In this paper we have presented an efficient method for the third virial coefficient with Kihara potential. For some of gases, example applications are given to demonstrate the effectiveness of the present formula. The results of calculation for the third virial coefficient with Kihara potential are in good agreement in the literature.

2. Definition and expansions relations for the third virial coefficient with Kihara potential

The virial equation of state expresses the deviation from ideal behavior of real gases and can be defined in the general series form

$$\frac{PV}{nRT} = Z = 1 + B_2(T) \frac{n}{V} + B_3(T) \frac{n^2}{V^2} + \dots, \quad (1)$$

which is expansion in powers of the number of molecules per unit volume n/V , $B_2(T)$, $B_3(T)$,... are called the second virial coefficient, the third virial coefficient and so on [12]. The virial coefficients depend only on temperature and potential energy of interaction between molecules. The third virial coefficient in terms of intermolecular potential $u(r_{ij})$ are given in the following forms

$$B_3(T) = -\frac{N_A^2}{3} \iiint f(r_{12}) f(r_{13}) f(r_{23}) dr_{12} dr_{13}, \quad (2)$$

$$f(r_{ij}) = \exp(u(r_{ij})/k_B T) - 1, \quad (3)$$

where $f(r_{ij})$ is Mayer functions, $u(r_{ij})$ is the intermolecular potential, N_A is Avogadro's constant, k_B is the Boltzmann constant and T is temperature. [12]. In this paper, for evaluation of the third virial coefficient, we have used the Kihara potential for molecules with spherical cores in the following form:

$$u(r) = \begin{cases} \infty & r < 2a \\ 4\varepsilon \left(\left(\frac{\sigma - 2a}{r - 2a} \right)^{12} - \left(\frac{\sigma - 2a}{r - 2a} \right)^6 \right) & r \geq 2a \end{cases}, \quad (4)$$

where a is the radius of spherical molecular core, ε is the depth of the potential well, σ is the collision diameter, and r is the distance between the particles [4, 12].

In this section, for evaluation of third virial coefficient with Kihara potential, the three body systems are illustrated in Fig. 1.

Figure 1. The interaction of three atoms

From the Fig. 1, the relations between of parameters r_{12} , r_{13} and r_{23} can be obtained from as

$$|r_{13} - r_{12}| = r_{23} = \sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13} \cos \varphi}, \quad (5)$$

$$dr_{13} = 4\pi r_{13}^2 dr_{13}, \quad (6)$$

$$dr_{12} = 2\pi r_{12}^2 dr_{12} \sin \varphi d\varphi, \tag{7}$$

The substituting Eq. (5)-(7) into the Eq. (2), we have obtained the following formula

$$B_3(T) = 8\pi^2 \frac{N_A^2}{3} \left[\int_0^\infty r_{12}^2 f(r_{12}) \int_0^\infty r_{13}^2 f(r_{13}) \int_{-1}^1 f\left(\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta}\right) d\eta dr_{12} dr_{13} \right]. \tag{8}$$

We have obtained the following form for third virial coefficient

$$B_3^*(T^*) = \frac{6}{(1+a^*)^6} \left[\int_0^\infty \left(e^{-\frac{4}{T^*} \left((r_{12}^* - a^*)^{-12} - (r_{12}^* - a^*)^{-6} \right)} - 1 \right) \int_0^\infty \left(e^{-\frac{4}{T^*} \left((r_{13}^* - a^*)^{-12} - (r_{13}^* - a^*)^{-6} \right)} - 1 \right) \right. \\ \left. \int_{-1}^1 \left(e^{-\frac{4}{T^*} \left(\left(\sqrt{r_{12}^{*2} + r_{13}^{*2} - 2r_{12}^* r_{13}^* \eta} - a^* \right)^{-12} - \left(\sqrt{r_{12}^{*2} + r_{13}^{*2} - 2r_{12}^* r_{13}^* \eta} - a^* \right)^{-6} \right)} - 1 \right) r_{12}^{*2} r_{13}^{*2} d\eta dr_{12} dr_{13} \right], \tag{9}$$

where, $B_3^*(T^*) = B_3(T^*)/b_0^2$, $b_0 = 2\pi N_A \sigma^3/3$, $T^* = k_B T/\varepsilon$, $r_{ij}/\sigma - 2a = r_{ij}^*$ and $2a/\sigma - 2a = a^*$

3. Numerical results and discussion

In this paper, we have presented an efficient formula for third virial coefficient using Kihara potential. The established formula is general and free of any restriction on its applications to gases. The Mathematica 7.0 international mathematical software has been used to calculate the formula obtained in this paper. The integrals in Eq. (9) have been evaluated by using numerical methods. The obtained results are compared with theoretical data and show a good agreement in the literature data [14]. The results of calculations of the third virial coefficient are presented in Tables 1-2 for $0.50 \leq T^* \leq 100$.

Table 1. The results of calculation for the third virial coefficient $B_3^*(T^*)$ by the collision diameter σ and the radius of spherical molecular core a

T^*	C_2H_6	C_3H_8	$C(CH_3)_4$	$n-C_5H_{12}$
0.50	-8.57673	-5.42229	-3.85708	-1.07265
0.80	0.553937	0.592589	0.590318	0.515087
1.00	0.566321	0.521352	0.487278	0.389782
2.00	0.338168	0.32441	0.317813	0.309801
3.00	0.327838	0.329057	0.331339	0.343681
4.00	0.33481	0.341493	0.346876	0.365788
5.00	0.340174	0.349509	0.356364	0.378317
6.00	0.342854	0.353753	0.361471	0.385215
10.00	0.339408	0.353223	0.362614	0.389901
100.00	0.217305	0.236729	0.249875	0.288048

Table 2. The results of calculation for the third virial coefficient by the parameter a^*

T^*	$a^* = 0.00$	$a^* = 0.05$	$a^* = 0.1$	$a^* = 0.5$	$a^* = 0.75$
0.50	-40.1638	-31.9503	-25.5726	-4.78344	-1.54602
0.80	-0.849145	-0.394662	-0.072073	0.593839	0.538579
1.00	0.429769	0.518713	0.569523	0.508616	0.411836
2.00	0.437073	0.417365	0.399518	0.321698	0.31028
3.00	0.352309	0.345039	0.339313	0.329788	0.340075
4.00	0.3266	0.325697	0.32567	0.343447	0.360938
5.00	0.315082	0.3176	0.32058	0.35205	0.372907
6.00	0.307625	0.312248	0.317037	0.35664	0.379477
10.00	0.286068	0.294367	0.302369	0.356765	0.383438
100.00	0.142535	0.154097	0.165289	0.241677	0.279047

The results of calculation from the Eq. (9) are plotted in Figure 2.

Figure 2. Third virial coefficient for Kihara potential

It is understood from the suitability of the graphics that the results are in good agreement with literature data [14].

The parameters of Kihara potential for gases C_2H_6 , C_3H_8 , $C(CH_3)_4$ and $n-C_5H_{12}$ are presented in Table 3 [4, 15].

Table 3. The parameters of Kihara potential

Molecules	a^* [4]	a^* [15]	$\sigma(A^\circ)$ [4]	$\sigma(A^\circ)$ [15]	$\varepsilon/k_B(^{\circ}K)$ [4]	$\varepsilon/k_B(^{\circ}K)$ [15]
C_2H_6	0.359	0.166	3.504	4.000	496.69	414.8
C_3H_8	0.470	0.168	4.611	4.519	501.89	493.7
$C(CH_3)_4$	0.551		5.762		557.75	
$n-C_5H_{12}$	0.818		5.029		837.82	

In conclusion, the obtained formula offers a direct and precise calculation advantage of the third virial coefficient for $0.50 \leq T^* \leq 100$ temperature range.

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