

## **Third Virial Coefficient and Compressibility Factors for Dense Spherical Gases Using the HFD-C Potential**

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### **Abstract**

Reduced third virial coefficients of several gases made of spherical molecules interacting with the HFD - C potential has been calculated as a function of the reduced temperature. A correlation equation  $C^*(T^*)$  For spherical gases is presented. Theoretical results have been compared with the experimental data for Ar, Kr, Xe, CH<sub>4</sub>, CF<sub>4</sub>, and SF<sub>6</sub>. Furthermore, the values of the compressibility factors have been obtained in the reduced temperature range  $1.5 \leq T^* \leq 10$  and reduced pressure range  $0.02 \leq P^* \leq 1.00$ . Satisfactory agreement is found between the theoretical and experimental results over the entire temperature and pressure range studied.

**Keywords:** *Virial Coefficient, Compressibility Factors, Dense Spherical Gases, HFD-C Potential*

### **Introduction**

The third virial coefficient,  $C(T)$ , which involves the simultaneous interaction of three molecules, is considerable importance. Firstly, because it is relatively more sensitive to the potential energy function, thereby allowing a sever test of an assumed model, and secondly since it yields quantitative thermodynamic information at high densities.

Several authors have calculated the third virial coefficient of spherical gases using simple potential models: hard sphere (Hirschfelder *et al.*, 1964); square well, Kihara, exp. - 6 sutherland (Sherwood and prausnitz, 1964); Lennard - Jones (Sherwood and prausnitz, 1964; Bird *et al.*, 1950; Ree and

Hoover, 1964). A number of authors have calculated the third virial coefficient of non-spherical molecules by introducing an addition angle dependent term in the potential energy function plus a Lennard - Jones (12,6) model representing the spherical contribution of pair interaction (Stogryn, 1968; Singh and Singh, 1976).

For the spherically symmetric potential, Aziz and Chen (1977) have proposed six models: HFD - A, HFD-B, HFD-C, HFD-D, HFD-I, and HFD-II, which are in satisfactory agreement with experimental results. They preferred HFD-C in moderate and high temperature upon comparison of theoretical and experimental results. It can be shown that the second virial coefficient of gases composed of molecules interacting with the HFD-C potential model provides an excellent agreement with the experimental results (Boushehri *et al.*, 1987; Boushehri and Maghari, 1990; Boushehri and Maghari, 1992).

The purpose of the present work is to calculate the third virial coefficient of a gas composed of spherical molecules (Ar, Kr, Xe, CH<sub>4</sub>, CF<sub>4</sub>, and SF<sub>6</sub>) interacting with the potential having the same shape as the HFD-C potential of Aziz and Chen (1997) for Ar - Ar interaction, but should be regarded here simply as a realistic general model for U(r). We propose the formulas for the third virial coefficients by different expressions in different temperature regions. The results of the third virial coefficient of HFD-C gases are the used for predicting the compressibility factor in the reduced temperature range  $1.5 \leq T^* \leq 10$  and reduced pressure range  $0.02 \leq P^* \leq 1.00$ . In this paper, the effect of non-additivity of potential is neglected.

### Calculations

The statistical Mechanical expression for the reduced third virial coefficient is explicitly given by (McQuarrie, 1976).

$$C(T) = -\frac{1}{3V} \iiint f_{12} f_{13} f_{23} dr_1 dr_2 dr_3 = -\frac{1}{3} \iint f_{12} f_{13} f_{23} dr_{12} dr_{13} \quad (1)$$

where the Mayer function  $f_{ij}$  is defined as

$$f_{ij} = \exp(-u_{ij}) - 1 \quad (2)$$

with  $\beta = 1/kT$  and  $u_{ij} = u(r_{ij})$  representing the intermolecular potential function. In the expression of  $C(T)$ , the force between any two molecules is assumed to be independent of the location of the third molecule.

In our calculation the form chosen for  $u(r)$  is

$$u^*(x) = Ax^2e^{-\alpha x} - \left(\frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}}\right)F(x) \quad (3)$$

where

$$x = \frac{r}{r_m}, u^* = \frac{u}{(\epsilon/k)}$$

$$F(x) = \exp\left[-\left(\frac{1.4}{x} - 1\right)^2\right] \quad x < 1.4 \quad (3a)$$

$$F(x) = 1 \quad x \geq 1.4$$

and

$$A = 9.502720 \times 10^6$$

$$\alpha = 16.345655$$

$$C_6 = 1.0914254$$

$$C_8 = 0.6002595$$

$$C_{10} = 0.3700113$$

$$r_m/\sigma = 1.119629$$

Here  $r_m$  is the position of the potential minimum,  $\sigma$  is the value of  $r$  for which  $u(r) = 0$ , and  $\epsilon$  is the depth of the potential well. This potential has the same shape as HFD - C potential of Aziz and Chen for Ar - Ar interaction, but should be regarded simply

as a realistic general model for  $u(r)$ . If we define a reduced third virial coefficient as:

$$C^*(T^*) = \frac{C(T)}{b_0^2} \tag{4}$$

where  $b_0 = \frac{2\pi N^2}{3}$  is the hard sphere second virial coefficient, then

$$C^*(T^*) = -\frac{3}{4\pi^2} \iint f_{12} f_{13} f_{23} dr_{12}^* dr_{13}^* \tag{5}$$

where the reduced temperature,  $T^*$ , and reduced distance,  $r^*$ , are defined as:

$$T^* = \frac{T}{(\epsilon/k)} \text{ and } r^* = \frac{r}{\sigma} \tag{6}$$

Substituting eqs. (3) and (4) in eq. (5) the reduced third virial coefficient can be evaluated numerically.

**Results and Discussion**

Table 1 lists the values of  $C^*(T^*)$ ,  $C'^*(T^*)$  and  $C''^*(T^*)$  in the reduced temperature rang  $0.7 \leq T^* \leq 300$ , where  $C'^* = dC^*/dT^*$  and  $C''^* = d^2C^*/dT^{*2}$ . Figure 1 shows the correlation curve for  $C^*(T^*)$ .

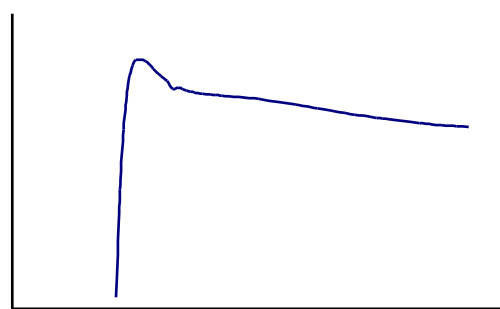
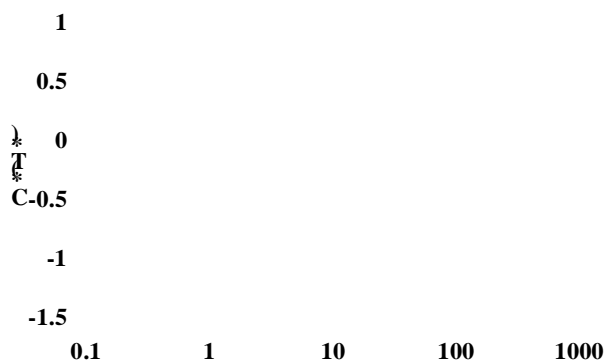


Figure 1- Correlation curve for  $C^*(T^*)$ .



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**Table I. A tabulation of the reduced third virial coefficient and its derivatives for the HFD - C potential**

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$T^*$	$C^*(T^*)$	$C^{*'}(T^*)$	$C^{*''}(T^*)$
0.70	-1.40575	16.88	-140
0.75	-0.49300	10.11	-86.9
0.80	0.02068	6.106	-55.4
0.85	0.31174	3.667	-36.0
0.90	0.47492	2.145	-23.7
0.95	0.56303	1.178	-15.8
1.00	0.60649	0.556	-10.5
1.05	0.62322	0.1553	-6.87
1.10	0.62403	-0.1033	-4.41
1.15	0.61553	-0.2679	-2.70
1.20	0.60179	-0.3699	-1.51
1.25	0.58536	-0.4300	-0.673
1.30	0.56780	-0.4619	-0.086
1.40	0.53278	-0.4717	0.608
1.45	0.51625	-0.4663	0.801
1.50	0.50067	-0.4524	0.928
1.55	0.48610	-0.4352	1.01
1.60	0.47259	-0.4160	1.05
1.65	0.46010	-0.3958	1.07
1.70	0.44858	-0.3753	1.07
1.75	0.43800	-0.3550	1.06
1.80	0.42828	-0.3352	1.04
1.85	0.41935	-0.3161	1.01
1.90	0.41117	-0.2979	0.97
1.95	0.40366	-0.2805	0.94
2.00	0.36676	-0.2641	0.903
2.10	0.38462	-0.2340	0.827
2.20	0.37436	-0.2075	0.753
2.30	0.36566	-0.1843	0.683
2.40	0.35825	-0.1640	0.618
2.50	0.35192	-0.1464	0.558
2.60	0.34649	-0.1310	0.503
2.70	0.34180	-0.1176	0.454
2.80	0.33774	-0.1060	0.409
2.90	0.33420	-0.0959	0.369
3.00	0.33110	-0.0871	0.333
3.50	0.32013	-0.0578	0.199
4.00	0.31346	-0.0436	0.119
4.50	0.30875	-0.0374	0.071
5.00	0.30494	-0.0354	0.041
10.0	0.27496	-0.0558	0.017
20.0	0.22866	-0.0749	0.061
30.0	0.19751	-0.0775	0.078
40.0	0.17536	-0.0762	0.084
50.0	0.15861	-0.0738	0.087
60.0	0.14538	-0.0712	0.087
70.0	0.13460	-0.0686	0.086
80.0	0.12559	-0.0662	0.085
90.0	0.11792	-0.0640	0.084
100	0.11129	-0.0619	0.082
200	0.07339	-0.0474	0.068
300	0.05584	-0.0338	0.052
400	0.04534	-0.0392	0.059
500	0.03847	-0.0303	0.047

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However, it is convenient for curve - fitting purpose to divide the temperature range into three parts. The results for the reduced third virial coefficient are as follow:

$$C^* = 0.6069 + 0.5611(\ln T^*) - 5.104(\ln T^*)^2 + 11.91(\ln T^*)^3 - 15.39(\ln T^*)^4 + 2.899(\ln T^*)^5 \quad 0.7 \leq T^* \leq 1.15 \quad (7a)$$

$$C^* = 0.6369 + 0.0893(\ln T^*) - 2.152(\ln T^*)^2 + 3.735(\ln T^*)^3 - 2.899(\ln T^*)^4 - 0.1640(\ln T^*)^5 \quad 1.15 \leq T^* \leq 6 \quad (7b)$$

$$C^* = 0.3409 - 7.82 \times 10^{-3} T^* + 1.3 \times 10^{-4} T^{*2} - 9 \times 10^{-7} T^{*3} \quad T^* > 6 \quad (7c)$$

Figure 2 compares the calculated and experimental third virial coefficients for Ne, Ar, Kr, Xe, CH<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub>. The two scaling parameters ε and σ may be obtained from the dilute gas viscosity data by a method discussed elsewhere (Clancy and Rigby, 1975; Maghari *et al.*, 1995, 1996, 1998, and 1999, Behnejad and Maghari, 1995; Haghghi and Maghari, 1997). The values of third virial coefficients reported by different authors differ from each other considerably. In view of these uncertainties, a reasonably good agreement between theory and experiment is found. Selected experimental data are taken from the critical survey of Dymond and Smith (1980).

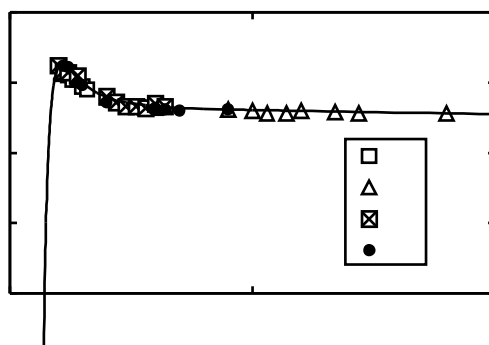
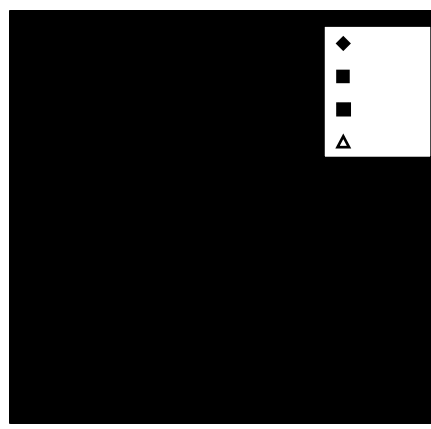
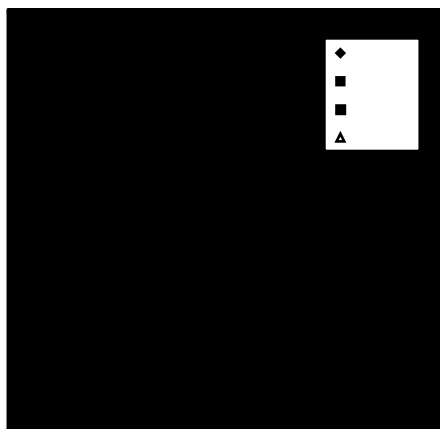


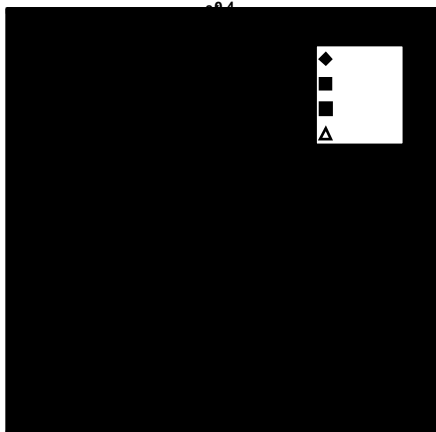
Figure 2 – A comparison between calculated and experimental third virial coefficients for Ne, Ar, Kr, Xe, CH<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub>.



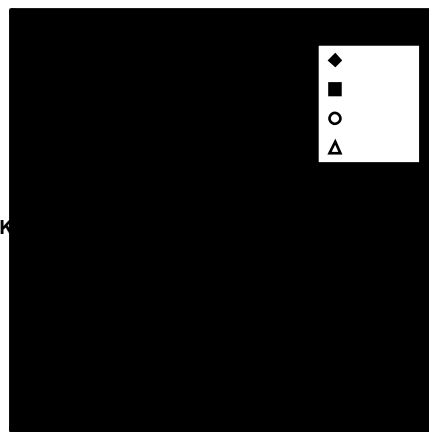




100 atm



600  
Temperature K



1.2  
1  
0.8  
0.6  
0.4  
0.2  
0  
0

200 400 600 800 1000

10 atm  
60 atm  
300 atm  
100 atm

0.8  
0.7  
0.6  
0.5  
0.4  
0.3  
0.2  
0.1  
0  
0



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Figure 3 - Deviation plots of the compressibility factors of Ne (a), Ar (b), Kr (c) and Xe (d).

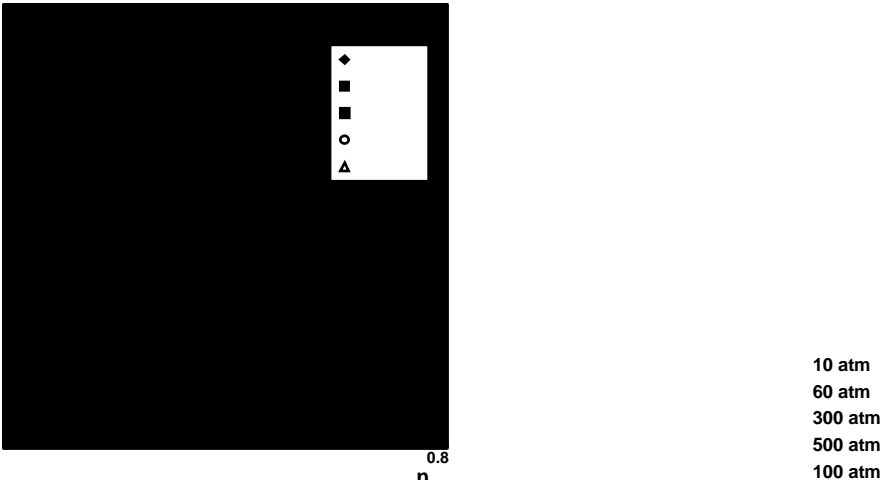


Figure 4 - Deviation plots of the compressibility factors of CH<sub>4</sub>.

**Conclusion**

The third virial coefficients of some spherical gases have been calculated by using the HFD - C potential energy function, and a correlation equation for  $C^*(T^*)$  is presented. The good agreement between the theoretical and experimental results indicates that the potential model used, in this work, is very accurate. In fact it is also severe test of the potential model, since the third virial coefficient is very sensitive to the potential energy function.

The compressibility factors for Ar, Kr, Xe, CH<sub>4</sub>, CF<sub>4</sub>, and SF<sub>6</sub> obtained in the reduced temperature range  $1.5 \leq T^* \leq 10$  and reduced pressure range  $0.02 \leq P^* \leq 100$ . The good agreement with the experimental data indicates that the presented equation of state underlying eqs. (7a)- (7c) is accurate.

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