THIRD VIRIAL COEFFICIENT IN NONPOLAR GASES AND THEIR MIXTURES

N. A. Zykov, R. M. Sevast'yanov,
and R. A. Chernyavskaya

UDC 536.75

Approximations are given for the additivie and nonadditive components of the third virial coefficient for the interaction potential (12-7, δ). The results are compared with experiment.

The classical third virial coefficient can be written in the form [1, 2]

$$C(T) = (b_0)^2 [C^*_{\text{add}}(T^*, \delta) + \nu^* \Delta C^*_{\text{nonadd}}(T^*, \delta)], \tag{1}$$

where $C^*_{\text{add}}(T^*, \delta)$ is the additive part and $\Delta C^*_{\text{nonadd}}(T^*, \delta)$ is the nonadditive part (in the above units) and $\nu^* = \nu/\varepsilon\sigma^9$ is the coefficient of the nonadditive three-particle interaction potential.

It has been established [1-3] that for spherically symmetric molecules the dominant part of the nonadditive three-particle interaction potential is given by the three-dipole London term (Midzuno and Kihara potential)

$$\Delta\varphi_{123} = \nu [1 + 3\cos\theta_{12}\cos\theta_{13}\cos\theta_{23}] (r_{12}r_{13}r_{23})^{-3}, \tag{2}$$

where r_{ij} and θ_{ij} are the sides and internal angles of a triangle formed by the three interacting molecules. The factor ν determines the strength of the potential, and to a good approximation one can take

$$\nu = \frac{3}{4}\alpha c_6, \tag{3}$$

where α is the polarizability and c_6 is the London dipole—diploe interaction coefficient.

For multiatomic molecules, Sherwood and Pauznitz [3] have suggested the following modification of the Midzuno and Kihara potential (2):

$$\Delta\varphi_{123} = -\frac{3}{4}\alpha \frac{\Sigma\varphi^{(2)}_{ij}}{\Sigma r_{ij}^{-6}} (1 + 3\cos\theta_{12}\cos\theta_{13}\cos\theta_{23}) (r_{12}r_{13}r_{23})^{-3}, \tag{4}$$

where φ^2_{ij} corresponds to the attractive energy in the pairwise interaction potential for multiatomic molecules. For spherically symmetric molecules

$$\Sigma\varphi^{(2)}_{ij}/\Sigma r_{ij}^{-6} = -c_6 \tag{5}$$

and (4) reduces to (2).

TABLE 1. Additive and Nonadditive Components of the Third Virial Coefficient of Argon, Nitrogen, and Methane C, $cm^6/mole^2$

T, K	Argon			Nitrogen			Methane		
	C_{add}	ΔC_{nonadd}	C	C_{add}	ΔC_{nonadd}	C	C_{add}	ΔC_{nonadd}	C
148,15	1248	1032	2280	1683	1119	2802	—2396	6415	4019
173,15	1275	705	1980	1480	789	2269	+1105	3770	4875
198,15	1160	526	1686	1300	603	1903	1854	2534	4388
223,15	1043	416	1459	1171	485	1656	1905	1858	3763
248,15	948	343	1291	1083	405	1488	1784	1445	3229
273,15	877	291	1168	1023	347	1370	1637	1172	2809
298,15	823	253	1076	982	304	1286	1505	981	2486
323,15	783	223	1006	955	269	1224	1396	841	2237
348,15	753	200	953	936	243	1179	1309	735	2044
373,15	730	181	911	924	221	1145	1240	652	1892
398,15	713	165	878	916	203	1119	1187	585	1772
423,15	701	152	853	912	186	1098	1144	531	1675

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 3, pp. 447-451, March, 1983. Original article submitted August 14, 1981.

0022-0841/83/4403-0312$07.50

TABLE 2. Coefficients for Approximations of C^*_{add} and C^*_{nonadd} at T* = 0.45 - 3.0

k	$\beta_0^{(3)}$	$\beta_1^{(3)}$	$\beta_2^{(3)}$	$\beta_3^{(3)}$
0	0,365647 (0)	0,298297 (0)	—0,599578 (—1)	—0,335922 (—1)
1	—0,376386 (0)	—0,630623 (0)	0,754467 (0)	0,370504 (0)
2	0,898883 (0)	—0,110346 (1)	—0,254279 (0)	0,295476 (0)
3	—0,425433 (0)	0,105637 (1)	—0,871698 (0)	0,300194 (0)
4	0,529373 (—1)	—0,131574 (0)	0,109271 (0)	—0,433315 (—1)
5	—0,420436 (—2)	0,106424 (—1)	—0,904796 (—2)	0,386160 (—2)
6	0,136163 (—3)	—0,349088 (—3)	0,301149 (—3)	—0,133431 (—3)

k	$\beta_0^{(4)}$	$\beta_1^{(4)}$	$\beta_2^{(4)}$	$\beta_3^{(4)}$
0	0,492110 (—1)	0,580741 (—1)	—0,623777 (—1)	0,565189 (0)
1	0,138170 (1)	0,199880 (1)	0,127598 (1)	0,412141 (1)
2	0,631198 (0)	0,349808 (0)	0,419032 (0)	0,309034 (0)
3	0,132882 (0)	0,978673 (—1)	—0,114492 (0)	—0,216422 (0)
4	—0,667733 (—2)	—0,185340 (—1)	0,222499 (—1)	0,268218 (—1)
5	0,510185 (—3)	0,186735 (—2)	—0,244518 (—2)	—0,257586 (—2)
6	—0,166480 (—4)	—0,698957 (—4)	0,939759 (—4)	0,996887 (—4)

Note. The coefficients are given in normalized form.

TABLE 3. Coefficients for Approximations of C^*_{add} and ΔC^*_{nonadd} for T* = 3.0 - 12

k	$\beta_0^{(3)}$	$\beta_1^{(3)}$	$\beta_2^{(3)}$	$\beta_3^{(3)}$
0	0,175183 (0)	0,328786 (0)	—0,105061 (0)	0,486291 (0)
1	0,237031 (1)	—0,222200 (1)	0,580473 (1)	—0,138505 (2)
2	—0,180669 (2)	0,141568 (2)	—0,655627 (2)	0,155089 (3)
3	0,765338 (2)	—0,713157 (2)	0,360430 (3)	—0,812465 (3)
4	—0,184284 (3)	0,188440 (3)	—0,101161 (4)	0,222256 (4)
5	0,239059 (3)	—0,255693 (3)	0,141393 (4)	—0,306582 (4)
6	—0,128782 (3)	0,140752 (3)	—0,785648 (3)	0,169010 (4)

k	$\beta_0^{(4)}$	$\beta_1^{(4)}$	$\beta_2^{(4)}$	$\beta_3^{(4)}$
0	0,118969 (—1)	0,288297 (—1)	—0,920101 (—1)	0,209942 (0)
1	0,174649 (1)	0,203824 (1)	0,510334 (1)	—0,567849 (0)
2	—0,130056 (1)	0,249290 (1)	—0,442357 (2)	0,748744 (2)
3	0,634374 (1)	—0,170651 (2)	0,243107 (3)	—0,437643 (3)
4	—0,115139 (2)	0,534351 (2)	—0,661435 (3)	0,123128 (4)
5	0,110843 (2)	—0,737421 (2)	0,854933 (3)	—0,162239 (4)
6	—0,426344 (1)	0,372089 (2)	—0,415448 (3)	0,797435 (3)

Note: The coefficients are given in normalized form.

TABLE 4. Comparison of Calculated values of the Third Virial Coefficients of a Helium-Nitrogen Mixture (upper row) with Experimental Data [10] (lower row), C_{ijk}, cm^6/mole^2

C_{ijk}	T, K					
	133,15	143,15	158,15	183,15	223,15	273,15
C_{111}	122 182	120 159	117 156	114 150	109 109	104 116
C_{112}	343 350	340 430	336 510	329 420	319 270	307 130
C_{122}	724 1020	713 750	701 590	688 780	674 750	662 690
C_{222}	3191 3100	2929 2920	2567 2414	2105 2132	1656 1636	1370 1416

If we use the Kihara–Midzuno–Kaneko expansion [5] as in the case of the pair potential (12-7, δ) [4], then for multiatomic molecules in the first approximation we can write

$$\varphi_{ij}^{(2)} = -c_6 r_{ij}^{-6}\left(1+\frac{5}{2}\frac{r_{eij}^2}{r_{ij}^2}+\ldots\right) = -c_6\left(r_{ij}^2-\frac{5}{6}r_{eij}^2\right)^{-3}. \tag{6}$$

Using the quasispherical model pair potential (12-7, δ) [4, 6] and the modified nonadditive three-particle Midzuno–Kihara potential given by (4) and (6), the additive and nonadditive components of the third virial coefficient were calculated numerically. The force constant of the interparticle interaction potential is given in [6], and in the calculation of ν^* we used a refined value of the coefficient ν [7]. The temperature dependence of the components of the third virial coefficients for argon, nitrogen, and methane is given in Table 1. At temperatures exceeding the Boyle temperature, the nonadditive component of the third virial coefficient is of about the same order as the additive component. The calculated values of the third virial coefficient agree with [8] within experimental error.

Numerical values of the components of the third virial coefficient obtained by direct integration are approximated by the formulas

$$C^*_{\mathrm{add}}(T^*,\ \delta) = \sum_{k=0}^{6}\sum_{j=0}^{3}\beta_j^{(3)}\delta^j\Delta^k, \tag{7}$$

$$\Delta C^*_{\mathrm{nonadd}}(T^*,\ \delta) = \sum_{k=0}^{6}\sum_{j=0}^{3}\beta_j^{(4)}\delta^j\Delta^k, \tag{8}$$

where $\Delta = \exp(1/T^*) - 1$; $\delta = (r_e/\sigma)^2$.

Values of the coefficients $\beta_j^{(3)}$ and $\beta_j^{(4)}$ for two temperature regions $T^* = 0.45 - 3.0$ and $T^* = 3.0 - 12$ are given in Table 2 and Table 3, respectively. For $\delta \leqslant 0.4$ the approximations (7) and (8) give the third virial coefficient with an error not exceeding 1% and its first and second derivatives with respect to temperature within errors of 5 and 20%, respectively. These errors are considerably smaller than those which typically result from differentiation of the smoothed experimental data.

For determination of the third virial coefficient in a gas mixture, it is necessary strictly speaking to perform a direct numerical calculation of the "mixed" third virial coefficients C_{ijk}. However, Rowlinson et al. [9] have shown that for the additive components of the "mixed" C_{ijk} one can use in the first approximation the same function $C^*_{\mathrm{add}}(T^*,\ \delta)$ but with different arguments. An extension of the approximation recommended in [9] to a multiatomic gas can be written in the form

$$a_{ijk} = \sqrt[3]{a_{ij}a_{ik}a_{jk}}, \tag{9}$$

$$\varepsilon_{ijk} = \sqrt[3]{\varepsilon_{ij}\varepsilon_{ik}\varepsilon_{jk}}, \tag{10}$$

$$\nu_{ijk} = \sqrt[3]{\nu_{iii}\nu_{jjj}\nu_{kkk}}, \tag{11}$$

$$r_{eijk}^2 = \frac{1}{3}\left(r_{eij}^2 + r_{ejk}^2 + r_{eik}^2\right), \tag{12}$$

and $a_{ijk} = \sqrt{\sigma_{ijk}^2 - r_{eijk}^2}$, $T^*_{ijk} = kT/\varepsilon_{ijk}$, $\delta_{ijk} = r_{eijk}^2/\sigma_{ijk}^2$.

As an example, Table 4 shows a comparison of the calculated values of the third virial coefficients C_{ijk} in a helium–nitrogen mixture and the experimental data [10]. The results are consistent within experimental error.

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THERMAL CONDUCTIVITY OF TRANSPOSED MULTISTRAND FLAT SUPERCONDUCTOR

W. Escher

UDC 536.21

Longitudinal and transverse thermal conductivities are calculated for a rectangular superconductor consisting of transposed multistrand wires.

Coils for superconducting magnets are often wound with transposed wires, each consisting of twisted superconducting strands embedded in a metal matrix. There are available transposed conductors with the space between strands completely filled by solder metal, in another version of such conductors the strands are only coated with solder metal or an oxide layer.

Inasmuch as such coils are cooled only at certain locations, information about the longitudinal thermal conductivity $\lambda_{\parallel}$ and the transverse thermal conductivity $\lambda_{\perp}$ is needed for an understanding of the processes of heat propagation along the conductor and heat transfer to cooling helium. These thermal conductivities have been calculated on the basis of the conductor model with solder metal between individual multistrand wires (Fig. 1).

Each of the quantities $\lambda_{\perp}$ and $\lambda_{\parallel}$ consists of two components λ_1 and λ_2 characterizing heat conduction through wire and solder, respectively, in directions perpendicular and parallel to the wires. Both λ_1 and λ_2 are determined not only by the thermal conductivity of the respective materials (wire and solder) but also by the coefficients of heat transfer between them and by the geometry of the conductor structure. Furthermore, $\lambda_{\perp}$ and $\lambda_{\parallel}$ depend on the transposition angle of wires in the conductor.

Thermal Conductivity of Composite Wire. In calculation of the thermal conductivity of a composite wire, it is permissible to disregard heat conduction through the superconductor, inasmuch as the thermal conductivity of the matrix material (copper) λ_M is approximately three orders of magnitude higher than the thermal conductivity of the superconducting material (NbTi) λ_C [1]. In effect, therefore, superconductor strands only reduce the total cross section for heat removal.

An expression for the transverse thermal conductivity λ_{M_1} of wire was derived on the basis of the model shown in Fig. 2. The section of a composite wire is subdivided into hexagonal structures with hexahedral superconductor strands at their centers so that the area for heat transfer decreases and the path of heat transfer becomes longer. When a characteristic element of the matrix is subdivided into four geometrical segments, A, B, C, D, then the sum of their thermal resistances will determine λ_{M_1}:

$$\lambda_{M1} = \frac{\pi}{2} A_1 \lambda_M, \tag{1}$$

Dresden University, German Democratic Republic. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 3, pp. 451-457, March, 1983. Original article submitted February 16, 1982.