THE SECOND VIRIAL COEFFICIENT OF A NON-ASSOCIATING GAS WITH ANISOTROPIC INTERACTIONS

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Received July 16th, 1979

The second virial coefficient in systems with permanent and induced multipole interactions was studied by using a statistical-thermodynamics correlation based on the perturbation theory of fluids. Several pair potential combinations of the Lennard-Jones function with different, subsequently more complex anisotropic contributions, were considered; the improvement in the description of intermolecular interactions due to these non-central contributions brought about an improvement in the interpretation of experimental data. The characteristic dependence of the parameters ε/k on σ at different temperatures was obtained for all of the three systems studied (Ar, CH_4 and CH_3F). It was found that if experimental values of the second virial coefficient of methyl fluoride are correlated by a relation derived from the Stockmayer potential, two sets of the ε/k and σ can be employed.

The second virial coefficient of a gas, $B(T)$, is of a considerable practical interest as a quantity which makes it possible to determine the state behaviour of moderately compressed gases; from a theoretical point of view, the second virial coefficient is a quantity whose form can easily be determined from the intermolecular pair potential.

For more complex (more realistic) potentials, values of $B(T)$ are most often calculated by the method due to Pople and Buckingham[1,2], which starts from older methods due to Lennard-Jones[3] and Stockmayer[4]. The theory by Pople and Buckingham is a perturbation method, which enables to calculate $B(T)$ if intermolecular interactions in the system studied are given as the sum of the Lennard-Jones 12–6 (LJ) and a perturbation potential. This perturbation potential contains most often contributions due to long-range anisotropic interactions (anisotropic-dispersion, multipole and induced interactions)[5–8].

In our work we used the Pople and Buckingham method for interpreting experimental values of the second virial coefficient of three real gases with interactions described by several different potentials and for studying the temperature dependence σ, ε/k of the reference system considered. A special attention was given to parameters of the Stockmayer potential employed for the correlation of experimental data on methyl fluoride; the study of the state behaviour of argon served as a verification of the method proposed.

THEORETICAL

If the mutual interaction of two molecules, 1 and 2, is given by the potential $u(r, \omega_1, \omega_2)$ (where $r = r_{12}$ is the distance between their centres of gravity and ω_1, ω_2 are spatial angles describing the angular orientation of the molecules), the second virial coefficient is given by the relation[9]:

$$B(T) = 2\pi N/\Omega_N \int_0^\infty \int_{\omega_1'} \int_{\omega_2'} \{1 - \exp[-\beta u(r, \omega_1, \omega_2)]\} r^2 \,\mathrm{d}r \,\mathrm{d}\omega_1 \,\mathrm{d}\omega_2 . \quad (1)$$

The angular-orientation average is performed over all possible mutual orientations of molecules (with the normalizing factor Ω_N); $\beta = 1/kT$. The total pair potential was considered as the sum of the Lennard–Jones and the perturbation potential, *i.e.*,

$$u(r, \omega_1, \omega_2) = u_{LJ}(r) + u_p(r, \omega_1, \omega_2) . \quad (2)$$

In our work we considered a polar gas, whose perturbation anisotropic interaction is given by the potential[5]

$$u_\mu = C\mu_1\mu_2 r^{-3}(2c_1c_2 + s_1s_2c_{12}) \quad (3)$$

and an octopolar polarizable gas, whose perturbation anisotropic interactions are given by the potentials[10,11]

$$u_\Omega = C\Omega_1\Omega_2 r^{-7} f_\Omega(c_1, c_2, s_1, s_2, c_{12}) , \quad (4)$$

$$u_{\alpha\Omega} = C(\alpha_1\Omega_2^2 + \alpha_2\Omega_1^2)\, r^{-10} f_{\alpha\Omega}(c_1, c_2, s_1, s_2, c_{12}) . \quad (5)$$

In these potentials, μ is dipole moment, Ω is octopole moment, α is dipole moment polarizability, $c_i \equiv \cos\Theta_i$, $s_i \equiv \sin\Theta_i$ $(i = 1, 2)$ and $c_{12} = \cos\Phi$ (the angles Θ, Φ describe angular orientations of axially symmetrical molecules). The functions f_Ω, $f_{\alpha\Omega}$ are complex angular-orientation functions, which are given explicitly in[10,11] and $C = (4\pi\varepsilon_0)^{-1}$ (where ε_0 is the permittivity in vacuum).

By inserting relation (*2*) into relation (*1*) and expanding the angular-orientation dependent part of the integrand into a series it follows:

$$B(T) = B_{LJ}(T) + \sum_{k=1}^{\infty} B_k(T) , \quad (6)$$

where the second virial coefficient of the LJ gas is given by the equation:

$$B_{LJ}(T) = 2\pi N \int_0^\infty \{1 - \exp[-\beta u_{LJ}(r)]\} r^2 \,\mathrm{d}r ; \quad (7)$$

contributions from the perturbation interactions to the total second virial coefficient are equal to

$$B_{\mathrm{k}}(T) = 2\pi N/(k!\Omega_{\mathrm{N}})(-\beta)^{\mathrm{k}} \int_0^\infty \int_{\omega_1'} \int_{\omega_2'} u_{\mathrm{p}}^{\mathrm{k}}(r, \omega_1, \omega_2) \exp\left[-\beta u_{\mathrm{LJ}}(r)\right] r^2 \,\mathrm{d}r \,\mathrm{d}\omega_1, \mathrm{d}\omega_2 \,. \tag{8}$$

To obtain explicit relations for the contributions $B_{\mathrm{k}}(T)$, it is firstly necessary to perform the angular-orientation average of powers of the perturbation potential. The following integration with respect to r was solved by Buckingham and Pople[2] by tabulating values of the dimensionless integrals

$$H_{\mathrm{n}}(y) = 12\sigma^{\mathrm{n}-3} y^4 \int_0^\infty r^{-(\mathrm{n}-2)} \exp\left[-\beta u_{\mathrm{LJ}}(r)\right] \mathrm{d}r \,, \tag{9}$$

where $y = 2(\varepsilon/kT)^{1/2}$ and σ, ε/k are parameters of the LJ potential. Values of the integrals $H_{\mathrm{n}}(y)$ can be obtained through the gamma function from the relation

$$H_{\mathrm{n}}(y) = y^{(27-\mathrm{n})/6} \sum_{t=0}^{\infty} \Gamma[(6t + n - 3)/12]\, y^t/t! \,. \tag{10}$$

The integration of relation (7) by parts yields the relation

$$B_{\mathrm{LJ}}(T) = -\tfrac{2}{3}\pi N\beta \int_0^\infty r^3 [\mathrm{d}u_{\mathrm{LJ}}(r)/\mathrm{d}r] \exp\left(-\beta u_{\mathrm{LJ}}(r)\right) \mathrm{d}r \tag{11}$$

which makes it possible to express also $B_{\mathrm{LJ}}(T)$ through $H_{\mathrm{n}}(y)$. By introducing

$$B^*(T) = 3B(T)/(2\pi N\sigma^3) \tag{12}$$

one can write

$$B^*_{\mathrm{LJ}}(T) = y^{-2}[\mathrm{H}_{12}(y) - \tfrac{1}{2}H_6(y)] \,. \tag{13}$$

By inserting potential (3) into Eq. (8) it is possible to derive[2] the following relation for contributions from the permanent dipole interaction to the total second virial coefficient of the polar gas:

$$B^*_{\mu\mathrm{k}}(T) = -y^{2\mathrm{k}-4} \left(\frac{(k/2)!}{2^{\mathrm{k}/2+1}(k+1)!}\right)^2 \left(\sum_{t=0}^{\mathrm{k}/2} (2t)!/(t!)^2\right) \mu^{*\mathrm{k}} H_{3\mathrm{k}}(y) \,, \tag{14}$$

where $k = 2, 4, 6, 8\ldots$

Anisotropic interactions in an octopolar polarizable gas are less pronounced. If they are to be included into the total virial coefficient in relation (*6*), it is sufficient to employ the first nonzero contributions ($B_{\Omega 1} = 0$), which are obtained[6,10] after replacing the perturbation potential in Eq. (*8*) with the sum of potentials (*4*), (*5*):

$$B^*_{\Omega 2}(T) = -\tfrac{297}{350}\Omega^{*4}\, H_{14}(y)\,, \tag{15}$$

$$B^*_{\alpha\Omega 1}(T) = -\tfrac{3}{5}y^{-2}\alpha^*\Omega^{*2}\, H_{10}(y)\,. \tag{16}$$

The reduced molecular parameters in Eqs (*14*)–(*16*) are given by the relations:

$$\mu^* = \mu/(C\varepsilon\sigma^3)^{1/2}\,, \quad \Omega^* = \Omega/(C\varepsilon\sigma^7)^{1/2}\,,$$
$$\alpha^* = \alpha/\sigma^3\,. \tag{17}$$

RESULTS

Relations (*13*)–(*16*) were employed to interpret the second virial coefficient of argon, methane and methyl fluoride. Smoothed values of $B(T)$ from ref.[12] were taken as experimental data (supplemented with several values reported also in ref.[12]).

TABLE I

Calculated and Experimental Values of the Second Virial Coefficient of Argon

The theoretical description employed: LJ gas with the parameters $\sigma = 3{\cdot}46 \,.\, 10^{-10}$m, $\varepsilon/k = 121{\cdot}5$ K. The parameters are to be used in the temperature range 90—783 K. The figures in parentheses are the difference between calculated and experimental values.

T K	B_{LJ} 10^{-6} m^3/mol	B_{exp} 10^{-6} m^3/mol
873·16	20·14 (0·66)	19·48 ± 0·2
773·16	17·80 (0·04)	17·76 ± 0·2
600·0	12·39 (—0·11)	12·50 ± 0·5
500·0	7·08 (—0·22)	7·30 ± 0·5
400·0	— 1·61 (—0·71)	— 0·90 ± 0·5
300·0	— 16·95 (—1·35)	— 15·60 ± 0·5
200·0	— 51·79 (—5·19)	— 46·60 ± 1
125·0	—125·96 (—2·46)	—123·50 ± 1
100·0	—185·73 (—0·23)	—185·50 ± 1
90·0	—223·91 (4·09)	—228·00 ± 1
85·0	—246·26[a] (9·74)	—256·00 ± 1
81·0	—267·94[a] (16·06)	—284·00 ± 1

[a] Values extrapolated with the given parameters σ and ε/k.

The parameters σ, ε/k were fitted to the experimental data by using the least squares method, the other molecular parameters were taken from literature.

Values of the integrals $H_n(y)$ were obtained during the computations by interpolating logarithms of $H_n(y)$ from Table I of ref.[2]. The mean deviation between values of the second virial coefficient calculated by this method and those calculated trough the gamma functions was estimated as 0·7%.

Tables I and II report calculated and experimental values of the second virial coefficient of argon and methane, for which the course of $B(T)$ is known with considerable accuracy in a wide temperature range. The resulting standard deviation is $\pm 2{\cdot}56 \,.\, 10^{-6}$ m^3/mol for argon (LJ gas), $\pm 3{\cdot}38 \,.\, 10^{-6}$ m^3/mol for methane (LJ gas) and $\pm 2{\cdot}18 \,.\, 10^{-6}$ m^3/mol for methane (octopolar polarizable gas). The temperature dependence of deviations between calculated and experimental values exhibits in all the three cases a characteristic course (see also ref.[13]). The calculated dependences $B(T)$ are less convex than the experimental data, the theoretical and experimental curves cross twice one another.

TABLE II

Calculated and Experimental Values of the Second Virial Coefficient of Methane

The theoretical descriptions employed: LJ gas with the parameters $\sigma = 3{\cdot}91 \,.\, 10^{-10}$ m, $\varepsilon/k = 149{\cdot}7$ K (B_{LJ}); octopolar polarizable gas with the parameters $\sigma = 3{\cdot}87 \,.\, 10^{-10}$ m, $\varepsilon/k = 143{\cdot}8$ K, $\Omega^* = 0{\cdot}280$, $\alpha^* = 0{\cdot}045(B_{\mathrm{OP}})$. The parameters are to be used in the temperature range 120—623 K. The figures in parentheses are the difference between calculated and experimental values.

T K	B_{LJ} 10^{-6} m^3/mol		B_{OP} 10^{-6} m^3/mol		B_{exp} 10^{-6} m^3/mol
623·16	10·80	(1·14)	10·95	(1·29)	9·66 ± 0·2
600·0	8·81	(0·31)	9·13	(0·63)	8·50 ± 1·0
573·16	6·63	(0·65)	6·70	(0·72)	5·98 ± 0·2
548·16	4·29	(0·40)	4·57	(0·68)	3·89 ± 0·2
500·0	— 1·37	(—0·87)	— 0·66	(—0·16)	— 0·50 ± 1
400·0	— 17·52	(—2·02)	— 16·61	(—1·11)	— 15·50 ± 1
300·0	— 46·93	(—4·93)	— 45·03	(—3·03)	— 42·0 ± 1
250·0	— 72·04	(—5·04)	— 69·90	(—2·90)	— 67·0 ± 1
200·0	—113·14	(—6·14)	—110·85	(—3·85)	—107·0 ± 2
160·0	—169·95	(—0·95)	—168·28	(0·72)	—169·0 ± 6
140·0	—214·66	(2·34)	—214·01	(2·99)	—217·0 ± 8
120·0	—280·27	(3·73)	—282·86	(1·14)	—284·0 ± 8
110·0	—325·97[a]	(18·03)	—331·66[a]	(12·34)	—344·0 ± 10

[a] Values extrapolated with the given parameters σ and ε/k.

The magnitude of the contribution from the octopole and induced interactions to the total second virial coefficient of methane amounts to approximately 10% at lower temperatures. (At 120 K, *e.g.*, $B_{LJ} = -253{\cdot}67 \,.\, 10^{-6}$ m^3/mol, $B_{\Omega 2} = -25{\cdot}91 \,.\, 10^{-6}$ m^3/mol and $B_{\alpha\Omega 1} = -3{\cdot}28 \,.\, 10^{-6}$ m^3/mol.) In lower parts of Tables I and II we report results which serve for estimating the computational accuracy during a moderate extrapolation into regions of low temperatures.

The ability of the description employed to interpret experimental data on $B(T)$ of the nonpolar gases considered at different temperatures was studied qualitatively by using parameter isotherms[9], *i.e.*, lines connecting parameters which are solutions to the equation $B(\sigma, \varepsilon/k) - B_{\mathrm{exp}} = 0$ at a given temperature. With accurate experimental data and an exact theoretical description of the intermolecular interactions, these curves should intersect each other at one point. It is obvious from Fig. 1 that at higher temperatures, the intersections of the parameter isotherms of argon are not too separated from one another. At lower temperatures, the intersections of the isotherms correspond with ever higher values of σ and lower values of ε/k. An equally analogous course of the parameter isotherms was obtained with both theoretical descriptions of methane, too.

Parameters in the Stockmayer potential, which have so far been published for polar gases in the literature[14], are not too realistic — for σ they are rather low and for ε/k they are rather high, respectively. (*E.g.*, the reported values of σ for halogen derivatives of methane are lower than the value for methane.) To these parameters then correspond extremely high values of contributions from the dipole moments interaction to the total second virial coefficient, which amount to 70–95% refs [15,16]).

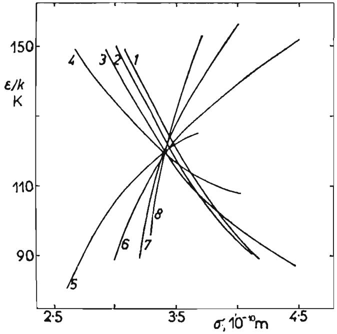

FIG. 1

Parameter Isotherms for the Lennard–Jones 12—6 Potential Obtained from Experimental Values of the Second Virial Coefficient of Argon

Temperatures: 90 K *1*, 125 K *2*, 200 K *3*, 300 K *4*, 500 K *5*, 600 K *6*, 773 K *7*, 873 K *8*.

Therefore we firstly investigated for methyl fluoride whether the problem of finding the potential parameters could possess more than one solution. It is obvious from Figs 2 and 3 that if values of $B(T)$ of methyl fluoride are interpreted through the LJ potential, only one pair of parameters σ and ε/k can be found, whereas there are two pairs of the parameters for the Stockmayer potential. At higher values of σ, the course of parameter isotherms in Fig. 3 is entirely analogous to that found for the LJ description; besides this fact, however, the isotherms intersect one another at a lower value of σ.

Values of the second virial coefficient calculated from parameters determined for both the LJ and the Stockmayer potential are given in Table III. Mean standard

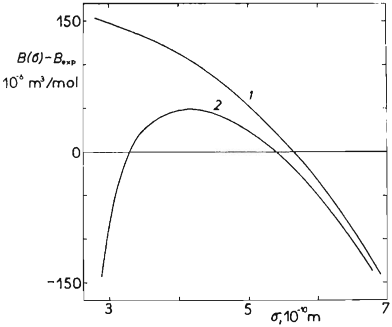

FIG. 2

The Solution of the Equation $B(\sigma) - B_{exp} = 0$ for Methyl Fluoride at $T = 320$ K, $B_{exp} = -174{\cdot}0 \,.\, 10^{-6}$ m^3/mol, $\varepsilon/k = 173{\cdot}1$K

Values of $B(\sigma)$ were calculated from: the Lennard-Jones 12—6 potential 1, the Stockmayer potential 2.

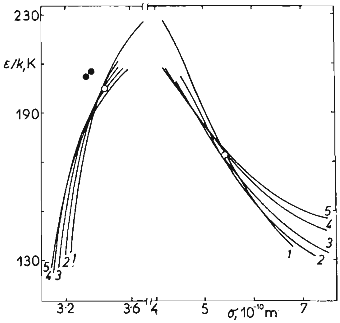

FIG. 3

Parameter Isotherms for the Stockmayer Potential Obtained from Experimental Values of the Second Virial Coefficient of Methyl Fluoride

Temperatures: 280 K 1, 320 K 2, 360 K 3, 400 K 4, 420 K 5. ● parameters from ref.[2,15], ○ parameters from this work.

deviations of the computations are $\pm 5{\cdot}01 \,.\, 10^{-6}$ m^3/mol (LJ gas), $\pm 4{\cdot}31 \,.\, 10^{-6}$ m^3 : : mol (S1 Stockmayer gas) and $\pm 1{\cdot}02 \,.\, 10^{-6}$ m^3/mol (S2 Stockmayer gas).

The parameters for the S2 description, which are close to those published earlier[2,14,15], yield a much higher value of the reduced dipole moment, a slower convergence of the perturbation expansion and a much higher contribution from the permanent dipole interaction to the total second virial coefficient than the parameters in the S1 description. At 280 K, *e.g.*, the contribution from the dipole interaction is in the first case approximately 71% ($\mu^* = 1{\cdot}754$, the contribution due to $B_{\mu 12}$, *etc.*, can be neglected), in the second case it is approximately 13% ($\mu^* = 0{\cdot}944$, and even $B_{\mu 8}$ can be neglected).

DISCUSSION

Results reported in Tables I–III show that the statistical-thermodynamics method outlined enables to interpret experimental data on real gases fairly well even though, except one case (values of B_{S2} in Table III), it could not correlate experimental values of the second virial coefficient within the range of reported errors. Computed $B(T)$ curves are less convex than experimental ones; both types of curves intersect twice each other.

The inclusion of long-range anisotropic interaction potentials improved the correlation of the experimental data of methane and methyl fluoride. For methyl fluoride we found that it is possible to use two pairs of parameters σ and ε/k for interpreting the experimental data on the second virial coefficient through the Stockmayer potential; low accuracy and a narrow range of the experimental data prevents us from

TABLE III

Calculated and Experimental Values of the Second Virial Coefficient of Methyl Fluoride

The theoretical descriptions employed: LJ gas with the parameters $\sigma = 5{\cdot}57 \,.\, 10^{-10}$ m, $\varepsilon/k = 178{\cdot}2$ K (B_{LJ}); Stockmayer gas with the parameters $\sigma = 5{\cdot}44 \,.\, 10^{-10}$ m, $\varepsilon/k = 173{\cdot}1$ K, $\mu^* = 0{\cdot}944(B_{S1})$; Stockmayer gas with the parameters $\sigma = 3{\cdot}43 \,.\, 10^{-10}$ m, ε/k 200·0 K, $\mu = 1{\cdot}754(B_{S2})$.

T K	$-B_{LJ}$ 10^{-6} m^3/mol	$-B_{S1}$ 10^{-6} m^3/mol	$-B_{S2}$ 10^{-6} m^3/mol	$-B_{exp}$ 10^{-6} m^3/mol
420·0	84·28	83·62	87·80	87·0 ± 2
400·0	97·94	98·04	99·35	99·0 ± 2
360·0	134·54	132·72	129·18	129·0 ± 3
320·0	177·67	177·90	173·21	174·0 ± 3
280·0	239·26	240·22	245·31	244·0 ± 3

making definite conclusions about the two descriptions. Due to the above mentioned arguments (the magnitude of the parameter σ of methane and its halogen derivatives, the magnitude of the contribution from the dipole interaction to the virial coefficient), the parameters of the S1 description can be considered as physically more realistic; they differ considerably from the methyl fluoride parameters published so far[2,14-16].

During the computations of parameter isotherms at lower temperatures and for all gases considered, we observed a shift in parameters σ and ε/k, corresponding to intersections of parameter isotherms, to higher values of σ and lower values of ε/k with decreasing temperature. This trend appeared approximately in the temperature region where the second virial coefficient should be sensitive (according to Klein and Hanley[17]) to the shape of the potential function ($T < 2\varepsilon_{LJ}/k$). This parameter shift is so pronounced and analogous for all the gases investigated, that it cannot be explained by low accuracy of the experimental data or of the computational process employed (or possibly by neglecting the quantum correction). The reason is most probably the imperfect description of the repulsion and dispersion interactions through the reference LJ potential. However, the lack of data is preventing one from using newly proposed more realistic functions, *e.g.*, the Kihara or Barker–Fisher–Watts[13,18] potentials, for the description of these interactions.

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Translated by K. Hlavatý.