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SECOND VIRIAL COEFFICIENT OF VAPORS

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An expression is offered for calculation of the second virial coefficient of vapors of nonassociative materials and their mixtures.

Much data from the literature was systematized and generalized in [1], and it was shown that for normal (nonassociated) materials, in accordance with the most recent generalizations, the second virial coefficient B can be expressed as a three-parameter function [2]:

$$B/V_c = F(T/T_c, A). \quad (1)$$

The structure of Eq. (1) reflects the three-parameter nature of the effective model potentials [3, 4]. It is significant that one and the same parameter A characterizes the individuality of the material in describing the properties of dense media (gases and liquids). This question was discussed in connection with the problem of multiparticle interactions in [1, 5].

Below we will consider the question of the second virial coefficient of vapors of multi-atomic mainly organic compounds. In the overwhelming majority of cases for vapor we need deal only with the relatively narrow dimensionless temperature range from 0.6 to 1.2. In this limited range of states the values of B are always negative, and the complex Eq. (1) in log-log coordinates $\log(-B) - \log T$ is practically a straight line. Therefore, it is possible to approximate Eq. (1) with the following simple expression:

$$-B/V_c = 1.241^{-1} (1.213 T_c / T)^m. \quad (2)$$

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TABLE 1. Values of B(T) for n-Hexane Calculated with Eq. (2)

T, K		320	340	360	380	400	420	440
$-B \cdot 10^3$ m ³ /kmole	[6]	1601	1352	1179	1017	897	796	709
	(2)	1596	1360	1172	1026	898	793	703

T, K		460	480	500	520	540	560	580	600
$-B \cdot 10^3$ m ³ /kmole	[6]	634	568	510	460	416	378	345	317
	(2)	627	592	506	457	415	378	345	318

In accordance with Eq. (1) the parameter m must be a unique function of the defining criterion A :

(3)

For known values of the critical parameters V_C , T_C , to use Eq. (2) it is necessary to select only the one parameter m . The quality with which Eq. (2) approximates experimental data may be judged from Table 1, which compares calculated results with generalized data recommended in [6] for n-hexane (n-hexane was also used as a test material in [1]). The results diverge from the literature by about the same amount (arithmetic mean approximately 0.005 m³/kmole) as the calculations with an interpolation expression containing five drive parameters in [6].

Equation (3) can be found by using the generalizing polynomials in [1]. It is preferable to define this function from experimental data for the 15 materials most deeply studied, including Barkan's latest effort [6]. We propose the following approximation:

$$m = 2.744 - 1.481 \lg A. \quad (4)$$

(use of a larger mass of data would probably produce a more accurate approximation). In Eq. (4) the parameter A is taken in accordance with the definition of [2]:

$$A = 100\pi \text{ for } T_C/T = 1.6, \quad (5)$$

where π is the dimensionless saturated vapor pressure. The deviations of experimental m values from Eq. (4) do not exceed ± 0.05 . Upon change in A from 4 (inert gases) to 1 (octane) m changes from 1.8 to 2.6. On the whole, the error in B determination with Eqs. (2) and (4) in the temperature interval indicated above, i.e., at $0.6T_C < T < 1.2T_C$, does not exceed the mean error of calculations with more complex expressions.

By using Eq. (4) one can perform a priori calculations of $B(T)$ on the basis of knowledge of a minimum set of parameters T_C , V_C , and A . These parameters can in turn be found from the structural formulas of the materials [7], allowing prediction of the second virial coefficient of the vapor.

Equation (2) is of most interest for describing the second virial coefficient of mixtures. In accordance with Eq. (2), the value of the parameter m in the analogous expression for the second cross-virial coefficient B_{12} [assuming that Eq. (2) is also valid for this case] can be found directly from the slope of the corresponding straight line in log-log coordinates

$$m_{12} = d \lg(-B_{12})/d \lg T. \quad (6)$$

The result is independent of the choice of V_C and T_C for the mixture, which is very significant, since it permits obtaining information on the combination rule for m and, correspondingly, for A . Unfortunately, the majority of experimental literature contains little information on $B_{12}(T)$ and Eq. (6) can only be used rarely. For other systems m_{12} must be determined from Eq. (2) in combination with the combination rules for V_C and T_C . Analysis of data from [8] was found to be in complete accord with the following combination rules:

$$V_{C12} = [(V_{C1}^{1/3} + V_{C2}^{1/3})/2]^3, \quad (7)$$

TABLE 2. Values of Complex b for Mixtures of Normal Hydrocarbons with Ethane. B, 10^{-3} m³/kmole

T, K	Ethane	Propane			n-Butane		
	$-B_1$	$-B_2$	$-B_{12}$	b	$-B_2$	$-B_{12}$	b
300	182	384,1	272,4	0,97	722,4	357,4	1,015
320	159	334,8	236,2	0,98	611,1	313,1	1,00
340	141	294,1	206,0	0,99	529,5	273,1	1,00
360	126	260,3	180,6	1,00	466,2	236,8	1,03

T, K	n-Pentane			n-Hexane		
	$-B_2$	$-B_{12}$	b	$-B_2$	$-B_{12}$	b
300	1176	426,7	1,08	1880	533,7	1,10
320	996	379,9	1,05	1601	462,6	1,09
340	852	336,2	1,03	1350	401,2	1,09
360	798	295,4	1,06	1163	347,8	1,10

$$T_{C_{12}} = (T_{C_1}T_{C_2})^{1/2} V_{C_1}V_{C_2}V_{C_{12}}^{-2}m_{12}^2/(m_1m_2), \quad (8)$$

$$m_{12} = (m_1 + m_2)/2. \quad (9)$$

The first of these expressions corresponds to a simple molecular model (see [7]); the second is a consequence of an expression relating the critical parameters to the dispersion interaction parameter C:

$$(T_C V_C^2/C)^{1/2} = 0.709 - 0.3583 \lg A \quad (10)$$

(see [7]) with consideration of the combination rule for C

$$C_{12} = (C_1 C_2)^{1/2}, \quad (11)$$

which follows from the pattern of additive atom-atom interactions, if we assume that $c_{ik} = c^{1/2}_i c^{1/2}_k$ [7]. In deriving Eq. (8) from Eq. (10), a correction term, the value of which does not exceed 0.3%, was omitted. Finally, Eq. (9) is the result of analyzing concrete experimental material. From Eq. (9) we obtain a combination rule for the defining similarity criterion A:

$$A_{12} = (A_1 A_2)^{1/2}. \quad (12)$$

The validity of rule (9) can be proved independently of Eq. (7) and (8), if we consider the relationship of B_{12} to B_1 and B_2 . If Eq. (9) is valid, then the complex

$$b \equiv (B_1 B_2)^{1/2} / (-B_{12}) \quad (13)$$

should not depend on temperature. Table 2 proves that this is in fact the case.

In accordance with the above, the cross-virial coefficient of mixtures B_{12} can be calculated with the expression

$$-B_{12}/V_{C_{12}} = 1.241^{-1} (1.213 T_{C_{12}}/T)^{m_{12}}, \quad (14)$$

using rules (7)-(9). Figure 1 compares the results of such calculations for 20 mixtures with experimental data from [8]. Each point on the figure corresponds to one material, and the majority of the data were obtained at 300°K. The mean-square deviation of the calculation results from the experimental values is 0.015 m³/kmole.

A unique feature of the combination rules employed in the present study which distinguishes them from those generally used (see [9]) is the form of Eq. (8) in which the value $T_{C_{12}}$ depends not only on T_{C_1} and T_{C_2} , but also on the other fundamental parameters. Use of this rule, which is a direct consequence of relationships relating the dispersion interaction constants, Eq. (11), allows a reduction in the mean-square error in calculating B_{12} by a factor of three times as compared to the rule recommended in [9], $T_{C_{12}} = T^{1/2}_{C_1} T^{1/2}_{C_2}$. We will stress that the proposed method requires no drive parameters characterizing the mixture, i.e., the fundamental cross parameters $V_{C_{12}}$, $T_{C_{12}}$, A_{12} can be calculated from the parameters of the pure components.

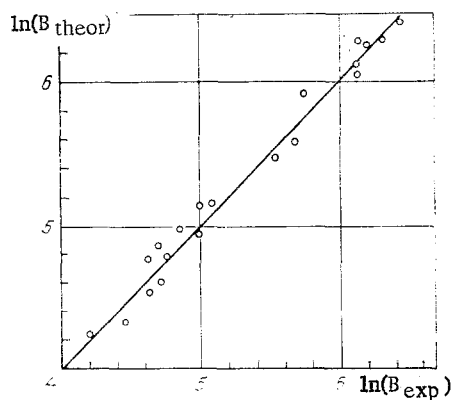


Fig. 1. Comparison of B_{12} (10^{-3} m³/kmole) calculated with Eqs. (2), (7)-(9) with experimental data in log-log scale.

On the phenomenological level the results obtained herein for B_{12} are an expression of a significant fact – the possibility of replacing interaction of two dissimilar multiatomic molecules by the effective interaction of identical ones. Analysis of this question by considering three-parameter model potentials of the spherical shell type confirm this conclusion. The details of this study will be the subject of a separate publication.

NOTATION

B , second virial coefficient; V_c , critical molar volume; T_c , critical temperature; A and m , defining thermodynamic similarity criteria [see Eqs. (4) and (5)]; C , molecular interaction dispersion constant; c_{ik} , corresponding atom-atom constants. Subscripts 1 and 2 indicate properties of first and second pure components, while subscript 12 characterizes corresponding parameters of the cross interaction.

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