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GENERALIZATION OF DATA ON THE SECOND VIRIAL COEFFICIENT OF GASES

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UDC 536.71

Generalization of empirical data for more than 30 substances (see Table 1) resulted in a relation for the second virial coefficient of normal substances. A single-parameter generalized law for the respective states is discussed.

Knowledge of general principles characterizing the behavior of the second virial coefficient of a large class of substances is necessary to obtain a single equation of state, to substantiate model potentials for the interaction of polyatomic molecules, and to determine the role of multiple-particle reactions in fluids. Two studies which have generalized data on the second virial coefficient are known. In [1], such a generalization was made for the class of normal (nonassociated) substances using a single-parameter generalized law for the corresponding states:

$$\frac{B}{V_B} = F_0\left(\frac{T_B}{T}\right) + \omega F_1\left(\frac{T_B}{T}\right), \tag{1}$$

where T_B and V_B are correction parameters; T_B is Boyle's temperature ($B(T_B) = 0$); V_B is a characteristic volume and is determined by the formula

$$V_B = T_B\left(\frac{\partial B}{\partial T}\right)_{T=T_B}. \tag{2}$$

The quantity ω in Eq. (1) is a unique characteristic of the substance — Pitzer's governing similitude criterion ("the acentric factor"). In [2], the generalization was done on the basis of broader empirical data: the author used new data for Ar and Kr (ω = 0), n-butane

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TABLE 1. Summary of Empirical Data Used to Generalize the Second Virial Coefficient

Formula of substance	Corrected temp. interval T_k/T	Value of ω	Error of generalization	Literature
Ar	0,1; 1,88	0	0,013	[6—11]
Kr	0,14; 1,95	0	0,005	[6, 10]
Xe	0,19; 1,32	0	0,013	[6, 10]
$CClF_3$	0,57; 1,57	0,178	0,050	[12,28]
CCl_2F_2	0,81; 1,61	0,176	0,069	[12]
CF_4	0,28; 1,12	0,187	0,067	[12, 28]
CH_2Cl_2	1,21; 1,68	0,204	0,202	[12]
$CHCl_3$	1,34; 1,70	0,204	0,187	[12]
CO	0,04; 1,46	0,048	0,181	[12]
CO_2	0,28; 1,50	0,207	0,066	[10, 12—19]
C_2H_4	0,60; 1,56	0,086	0,051	[12]
C_2H_6	0,49; 1,59	0,097	0,055	[12, 19]
Cyclopropane	0,99; 1,31	0,125	0,049	[12]
Propane	0,71; 1,63	0,144	0,027	[12]
C_3H_8	0,65; 1,75	0,149	0,045	[12, 20]
n-C_4H_{10}	0,73; 1,74	0,193	0,104	[12, 20]
iso-C_4H_{10}	0,80; 1,49	0,179	0,153	[12]
$(C_2H_5)_2O$	1,15; 1,67	0,273	0,422	[12]
n-C_5H_{12}	0,82; 1,72	0,246	0,195	[12, 20, 21]
iso-C_5H_{12}	0,97; 1,69	0,217	0,095	[12]
neo-C_5H_{12}	0,79; 1,47	0,194	0,069	[12]
C_6H_6	0,73; 2,01	0,257	0,157	[12, 22—24]
C_6H_{12}	0,96; 2,03	0,215	0,182	[12, 20]
n-C_6H_{14}	0,73; 1,70	0,298	0,168	[12, 20]
C_7H_8	1,01; 1,74	0,257	0,304	[12]
n-C_7H_{16}	0,77; 1,80	0,347	0,567	[12, 20,25,26]
n-C_8H_{18}	0,81; 1,91	0,39	0,233	[12, 20]
F_2	0,48; 1,44	0,068	0,054	[12]
N_2	0,09; 1,80	0,036	0,057	[10, 12, 19]
N_2O	0,73; 1,56	0,126	0,063	[12]
O_2	0,11; 1,93	0,020	0,091	[10, 12, 27]

(ω = 0.2), and n-octane (ω = 0.4). To describe B for substances with strongly polar molecules, a second governing criterion was introduced: the corrected dipole moment $\mu_R = 10^5\mu^2 P_k/T_k^2$. Unfortunately, the division of substances into polar and nonpolar was not done in the class of normal compounds, so that most of the polar compounds turned out to be associated substances and the generalization being discussed for normal substances is practically a single-parameter generalization (in the sense suggested above). Attempts were made in [3-5] to expand the single-parameter law for the corresponding states to polar and associated substances. The observation made previously also pertains to these studies.

Since these investigations were reported in the literature, a large number of studies containing new data on virial coefficients have appeared. The amount of data now known to exist is several times greater than the amount used in [2]. In connection with this, it would be useful to make a new generalization of the empirical material available.

This article uses data for more than 30 substances [6-28]. The total number of points is about 3000 (see Table 1). It should be noted that we dealt only with the literature contained in [6, 12]. In analyzing the data, weight factors inversely proportional to the squares of the absolute errors (according to authors' estimates) were introduced in some cases. In other cases, we adopted the factors used in [12].

The data was generalized on the basis of the formula

$$\frac{B}{V_k} = F_0\left(\frac{T_k}{T}\right) + \omega F_1\left(\frac{T_k}{T}\right). \tag{3}$$

We found ω by using a relation connecting this parameter with the governing criterion of thermodynamic similitude A:

$$\omega = 0.401 - 0.664 \lg A$$

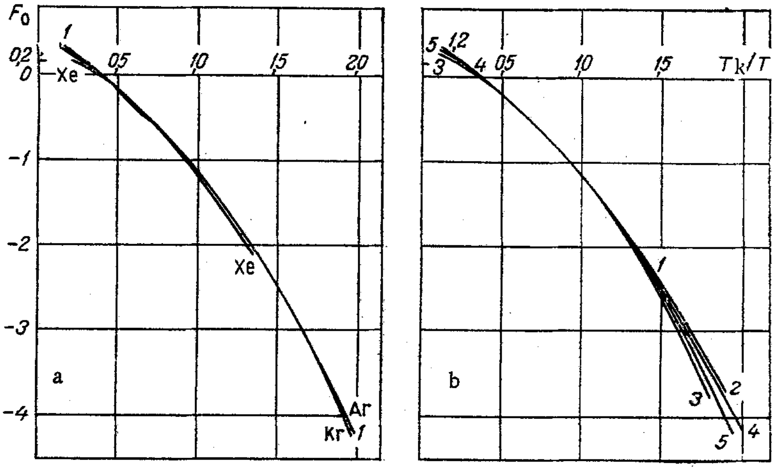

Fig. 1. Corrected temperature dependence of the second virial coefficient of the inert gases: a: 1) general curve for Ar, Kr, Xe (Eq. (7)); b: 1) Eq. (8); 2) (9); 3) (10); 4) (11); 5 (7).

with the value of A having been taken from [29]. (It was found that the addition of a term equal to the square of ω to Eq. (3) reduces the mean square error by 2%; thus, the third term of (3) proved insignificant and was not considered in the present work.) It should be pointed out that we chose the critical volume and temperature as the correction parameters, instead of the Boyle parameters in the Pitzer generalization [1]. Information on the critical parameters is more readily available, while the Boyle parameters are found from the second virial coefficient. Determining the Boyle parameters for most substances involves extrapolating results to a region which has not yet been investigated. Changing over to a more convenient normalization for the critical parameters allows us to obtain relations $V_k(V_B, \omega)$ and $T_k(T_B, \omega)$ on the basis of the new generalization (see below).

When $\omega = 0$, the function F_0 describes data for a group of inert gases. We used data from 252 points for three substances Ar, Kr, and Xe having small quantum corrections. We found $F_0(T_k/T)$ by the method of improved risk minimization [30]. A machine search was made for the form of F_0 as the sum of a set of functions arranged in the order of their significance. The search was made on a basis which included functions of the following form: normal and inverse functions, integral and rational functions (of the type $(2i - 1)/4$, $i = 1, \ldots$), temperature functions, $\ln\tau$, $\tau^{-1}\exp(\tau^2)$ $(\tau = T/T_k)$. The generalization was done separately for each of the three inert gases and for the three as a whole. The results are described by the formulas:

for Ar

$$F_0 = 0.450 - 1{,}017\,\tau^{-1} - 0{,}570\,\tau^{-2} - 0.0162\,\tau^{-5}, \tag{4}$$

for Kr

$$F_0 = 0.466 - 1{,}081\tau^{-1} - 0.535\,\tau^{-2} - 0{,}0177\,\tau^{-5}, \tag{5}$$

for Xe

$$F_0 = 0.500 - 1.101\tau^{-1} - 0.604\,\tau^{-2} - 0{,}0072\,\tau^{-5}, \tag{6}$$

for Ar, Kr and Xe

$$F_0 = 0.476 - 1.102\tau^{-1} - 0{,}528\tau^{-2} - 0{,}0171\,\tau^{-5}. \tag{7}$$

The standard deviations δ are 0.044, 0.011, 0.013, and 0.020, respectively.

The relations obtained are important for determining whether or not conditions of thermodynamic similitude are satisfied for monoatomic gases. If the potentials for the intermolecular reaction of these substances are determined by two known parameters rather than some larger number of parameters, the curves of $B/V_k(T_k/T)$ should be identical within their confidence interval. (As an approximate value of the confidence interval we took $3\sigma/\sqrt{N}$, where N is the number of points used for averaging. This value is 0.013, 0.004, and 0.005 for Ar, Kr, and Xe, respectively.)

Graphs of the functions (4)-(7) are shown in Fig. 1a. The standard deviations for the individual substances are 0.013 for Ar, 0.005 for Kr, and 0.013 for Xe. It can be seen that

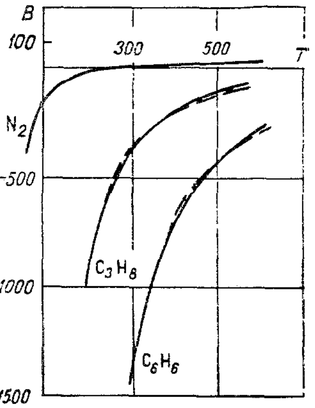

Fig. 2

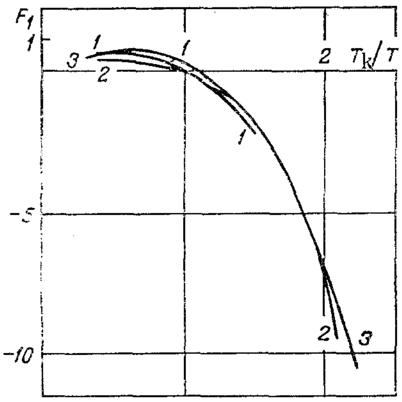

Fig. 3

Fig. 2. Temperature dependence of the second virial coefficient. The dashed curves represent literature data: N_2 [33], C_3H_8 [32]; C_6H_6 [34]; the solid lines are for Eqs. (3), (7) and (8), respectively. B, cm^3/mole; T, °K.

Fig. 3. Corrected temperature relation F_1: 1) Eq. (13); 2) (14); 3) (12).

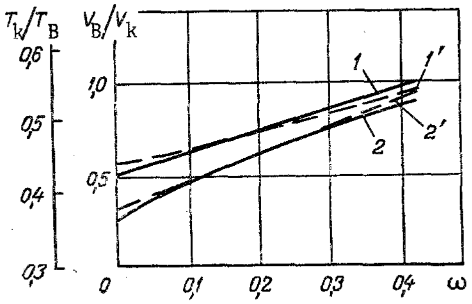

Fig. 4. Relations $V_B/V_k(\omega)$ and $T_k/T_B(\omega)$: 1) our data on $V_B/V_k(\omega)$; same on $T_k/T_B(\omega)$; 1' and 2') similar relations according to Pitzer [1].

the deviation observed for Xe determines the boundary within which we can speak of the thermodynamic similitude of the inert gases. Figure 1b compares generalizations for F_0 (curve 5) with available literature data: Pitzer [1] — curve 1 in the temperature range $T_k/T \in [0.26; 1.33]$

$$\frac{B}{V_k} = 0.492 - 1.124\tau^{-1} - 0.472\tau^{-2} - 0.0412\tau^{-3}; \tag{8}$$

Tsonopoulos [2] — curve 2 in the temperature range $T_k/T \in [0.26; 1.88]$

$$\frac{B}{V_k} = 0.492 - 1{,}124\tau^{-1} - 0.472\tau^{-2} - 0.0412\tau^{-3} - 0.0021\tau^{-8}; \tag{9}$$

Rabinovich [31] — curve 3 in the temperature range $T_k/T \in [0.12; 1.8]$

$$\frac{B}{V_k} = 0.349 - 0.139\tau^{-1} - 3.194\tau^{-2} + 3.319\tau^{-3} - 1.876\tau^{-4} + 0.367\tau^{-5}, \tag{10}$$

McGlashan [32] — curve 4 in the temperature range $T_k/T \in [0.17; 2.0]$

$$\frac{B}{V_k} = 0.430 - 0.886\tau^{-1} - 0.694\tau^{-2}. \tag{11}$$

The difference is significant at $T_k/T > 1.25$, i.e. the curves begin to diverge by an amount greater than 2σ for (7).

The function F_1 was determined by minimizing the functional

$$\Sigma W\left[\left(\frac{B}{V_k}-F_0\right)-F_1\omega\right]^2=\Sigma W\,(F_1^{\text{expt}}-F_1)^2\omega^2,$$

where the form of F_1, as the form of F_0, was chosen to be a four-term polynomial with the same degrees. As a result, we obtained the formula

$$F_1=0.257+2.016\tau^{-1}-2.577\tau^{-2}-0.132\tau^{-5}, \qquad (12)$$

which is valid in the temperature range $T_k/T \in [0.1;\ 2.0]$.

The standard deviation σ = 0.15. Figure 2 compares generalizations (3), (7), (8) with well-known results for N_2 [33], C_3H_8 [32] and C_6H_6 [34]. Figure 3 compares Eq. (1) for F_1 with the generalizations of Pitzer [1] in the temperature range $T_k/T \in [0.26;\ 1.33]$

$$F_1=0.434+1.145\tau^{-1}-1.881\tau^{-2}-0.346\tau^{-3}-0.0249\tau^{-8} \qquad (13)$$

and of Tsonopoulos [2] in the temperature range $T_k/T \in [0.25;\ 1.88]$

$$F_1=0.402-0.422\tau^{-1}+0.951\tau^{-2}-1.457\tau^{-3}-0.028\tau^{-8}. \qquad (14)$$

It should be noted that Eq. (12) is valid for a broader temperature range.

As was noted, a connection between the critical and Boyle parameters follows from the generalization obtained. Figure 4 shows the functions $T_k/T_B = f(\omega)$ and $V_B/V_k = g(\omega)$ found numerically on the basis of (3). Comparison with the analogous Pitzer curves [1] shows satisfactory agreement of both approximations. It also follows from Fig. 3 that the Pitzer generalization agrees satisfactorily with ours. This is particularly important because it was the Pitzer approximation that was used as a basis to verify the model three-parameter potentials in [35-38]. Thus, the conclusions reached in these works do not require significant revision.

More important is the general conclusion regarding the possibility of a single-parameter (one parameter ω) dimensionless description of the second virial coefficient. First let us explain the basis for this assertion. Of the 30 substances examined here, the data for 26 substances differs from the derived equation (3) by an amount which is within our error estimation δ. The deviation is no greater than 2δ for the other four substances. (However, the deviation from (3) is quite natural for substances with a relatively large dipole moment such as CH_3F, CH_3Cl, CH_2F_2, CHF_3, acetone, and methylformate, since these substances were not included in the generalization due to the small amount of corresponding empirical data available.)

It should be emphasized that the single-parameter character of the function $B/V_k(T_k/T, \omega)$ occurs for a group of substances which includes inorganic compounds (F_2, N_2, O_2, and oxides — NO_2, CO_2, CO), normal alkanes (from ethane to octane) and some of their isomers, alkenes (ethylene, propane), cyclic hydrocarbons (cyclopropane, cyclohexane), aromatic hydrocarbons (benzene), ethers (diethyl ether), halogenated hydrocarbons (freons, several methanes), etc.

The conclusion regarding the validity of the single-parameter generalized law for the corresponding states with regard to the second virial coefficient is very important in connection with molecular-kinetic interpretation of the conditions of thermodynamic similitude. The point is that the macroscopic parameter ω (as other "scales" of the thermodynamic similitude criterion [29]) is determined from information on the properties of a dense fluid [1, 29]. In principle, multiple-particle rather than pairwise molecular interactions occur in such a fluid. The second virial coefficient is determined only by pairwise interactions. It turns out that the contribution of multiple-particle interactions is not manifest in the form of a separate determining criterion. This can take place only in the case where the contribution is generally very small. The estimates available in the literature, however, do not provide grounds for believing such a conclusion to be valid. We should therefore seek an alternative explanation. Such an explanation can be obtained by analyzing the role of three-particle interactions on the basis of dispersive forces. The effect of the third molecule on the interaction between two molecules is realized through polarization of the third molecule by the pole of each of the other molecules and the action of the induced (virtual) dipole on the molecule-partner (the occurrence of additional polarization). The magnitude of the corresponding interaction is determined by the polarizability of the molecule and, in a dimensionless description, is determined by the ratio of the polarizability α to the critical volume V_k. This new governing criterion α/V_k does not change very much from one substance to another; the fact of the constancy of the ratio of α to the "natural" volume of the molecule is well known [39]. Thus, for alkanes, α/V_k is constant to within fractions of a percent. The relatively small role of the determining criterion α/V_k and the relatively small range of its variation explain the single-parameter character of the generalized law governing the corresponding states for both a dense fluid and for a slightly compressed gas.

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