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The Determination of the Second and Third Virial Coefficients from pVT-X Data of Binary Systems[1]

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The compressibility factor of multicomponent systems can be obtained in terms of virial coefficients of the pure components and their binary mixtures. This paper concerns a method with which, for that purpose, the second and third virial coefficients for these binaries have been determined from experimental data. From useful data, second and third virial coefficients are obtained as a quadratic function of the temperature. The density domain for which these results are applicable is discussed. When ample data are available, results for a sample mixture can be obtained in a straightforward manner. Nevertheless, it is shown that under much less favorable conditions—sometimes even when pure-component data are lacking—fairly good results can still be obtained. In that case, the choice for an appropriate combining rule has to be considered carefully. Finally, the involvement of ternary mixture data, both obtained experimentally and predicted by the equation, is considered.

KEY WORDS: compressibility; data analysis; mixtures; virial coefficients.

1. INTRODUCTION

It is a well-known fact that the compressibility factor of both pure gases and gas mixtures can be described conveniently within a fair density range with the simple relation,

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$$\begin{aligned} Z &= 1 + B\rho + C\rho^2 \\ Z &= \frac{pV}{RT} \\ V &= \frac{1}{\rho} \end{aligned} \tag{1}$$

in which p, V, R, and T denote, respectively, the pressure, molar volume, gas constant, and absolute temperature. The parameters B and C are commonly indicated as "second" and "third virial coefficients."

From statistical mechanics it is also known that the virial coefficients of an N-component mixture can be written as

$$\begin{aligned} B_{\text{mix}} &= \sum_{i,j}^{N} x_i x_j B_{ij} \qquad (B_{ii} = B_i) \\ C_{\text{mix}} &= \sum_{i,j,k}^{N} x_i x_j x_k C_{ijk} \qquad (C_{iii} = C_i) \end{aligned} \tag{2}$$

From Eq. (2), it can be seen that B_{mix} is determined completely by the second virial coefficient of the pure components and binary terms B_{ij}. In the case $N = 2$, C_{mix} is also determined by pure and binary terms; for $N > 2$, ternary terms are also present.

This paper concerns a method with which the binary terms have been determined from experimental data. The work was performed in order to obtain compressibility factors for natural gases, but the method is believed to have a general applicability.

2. METHOD

2.1. Pure Components

From Eq. (2), it is clear that, before getting started with binary systems, one first needs to obtain accurate data for the pure components. At this point, it is worthwhile to recapitulate the temperature dependences of the virial coefficients. These features are displayed graphically in Fig. 1. The units are arbitrary: a logarithmic temperature scale has been chosen, since the temperature dependence decreases rapidly at high temperatures. It can be seen that the coefficient B changes in sign at $\approx 2.7\ T_{\text{crit}}$ (the Boyle temperature) and shows only a shallow maximum at high temperatures. The third virial coefficient is clearly nonmonotonic, becomes positive at $\approx 0.7\ T_{\text{crit}}$, and has a pronounced maximum around $\approx 0.9\ T_{\text{crit}}$. In our work, the temperature dependence of B could be described perfectly as a

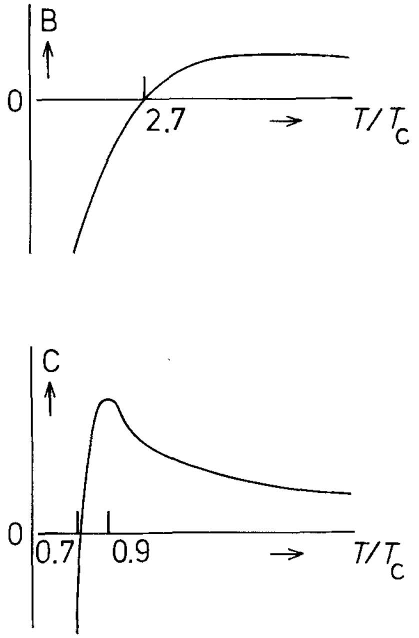

Fig. 1. The global temperature dependence of the second and third virial coefficient (T/T_c on logarithmic scale).

quadratic function of T. Due to the relatively short temperature interval considered in our work, a second-order fit for $C(T)$ could also be applied, despite the presence of the maximum.

The first step in the procedure was the recollection and evaluation of experimental data. From these, a selection was made with the following considerations.

(i) Only primary data for Z could be used; no smoothed values, results in parametric form, or values for virial coefficients already derived from experiments were taken into account,

(ii) The pressure and temperature range had to be within the desired range. As far as the pressure was concerned, only data up to the maximum *partial* pressure of the component in the mixtures which were to be considered (thus, in our case the natural gases) were needed. Within this range, a fair number of data points had to be available. Moreover, the conditions of pressure and temperature should be such that the system is not near the phase separation surface.

(iii) The accuracy quoted by the authors has to be sufficient.

The next step was a check of internal consistency of each data set. Data sets with conflicting results were discarded. For each isotherm in a data set, a least-mean-squares deviation fit with

$$Z = 1 + b\rho + c\rho^2$$

was made, without comparison of b and c with virial coefficients of other data sets. Once again, poor results justified the removal of the whole set. Finally, the best second-degree fits for b and c with the temperature were calculated. Here also, spurious results led to the removal of the data. After this screening procedure, final second-order functions $B(T)$ and $C(T)$ were determined from all remaining data for each pure component.

Of the natural gases considered, the most important constituent components are CH_4, N_2, CO_2, and C_2H_6; the temperature ranges from 270 to 330 K. Initially, pressures up to 80 bar were considered. Later, the upper limit was increased to 120 bar. The compressibility of the pure components can be predicted within 0.05% up to the relevant maximal partial pressures. As an example, the results for the virial coefficients of CH_4, being the most important component, are given in Table I. The first row gives the results for the analysis up to 80 bar; the second, for the last analysis up to 120 bar.

In the pressure range under consideration, it was possible to describe the compressibility factor within the experimental accuracy, taking only B's and C's into account. For instance, in the case of CH_4, the root mean square deviation is about 0.015% for a set of about 60 data points. In this example, the numbers are given with all significant digits. This suggests an accuracy which is much higher than commonly quoted for the virial coefficients, i.e., roughly $\approx 1\ \mathrm{cm^3 \cdot mol^{-1}}$ for B and $\approx 200\ \mathrm{cm^6 \cdot mol^{-2}}$ for C [1].

It must be emphasized that this does not mean that the virial coefficients have indeed been determined with a much higher accuracy. In fact, in our calculations, B and C are parameters which give a good prediction of the compressibility factor, provided that they are used *simultaneously*. It is not claimed that these coefficients are the same as the virial coefficients in the sense of statistical physics. Nevertheless, in Table I it can be seen that

Table I. Results for the Second and Third Virial Coefficients of CH_4 Obtained from Experimental Compressibility Data up to 80 and up to 120 bar[a]

0–80 bar	$B(273) = -53.37$; $B(298) = -42.77$; $C(273) = 2661$; $C(298) = 2406$
0–120 bar	$B(273) = -53.41$; $B(298) = -42.88$; $C(273) = 2677$; $C(298) = 2440$

[a] B in $\mathrm{cm^3 \cdot mol^{-1}}$; C in $\mathrm{cm^6 \cdot mol^{-2}}$.

the results for B are virtually independent of the pressure range condidered, while—even in the worst case—the change in C due to the extension of the pressure range is still an order of magnitude less than uncertainties generally quoted for third virial coefficients.

2.2. Binary Mixtures

According to Eq. (2), the virial coefficients for binary mixtures are given by

$$B_m = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \tag{3a}$$

$$C_m = x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222} \tag{3b}$$

In Eqs. (3a) and (3b), both cross terms and coefficients for the pure components are present. It is an essential feature of our work that, for the latter coefficients, only the results of the analysis described in the previous section have been substituted. Moreover, the experimental data for mixtures have always been obtained from other sources than for the pure components, even in the case that data for mixtures and pure components have been determined by the same experiments. The aim of this constraint is the diminution of the influence of systematic errors into the final results. Now that the coefficients for the pure components have been fixed, three coefficients are left to be determined from experimental data of binary mixtures. With each coefficient being described as a three-parameter function of the temperature, the results depend once more on nine parameters. Thus, in order to obtain a sensible fit, one needs ample data points, not only in the density and temperature range but also for a variety of compositions. Where possible, this parameter fitting has been performed. Again, only well-screened data have been used. The results for the pure components B and C were invariably substituted and the other parameters were calculated simultaneously by a least-mean-squares deviation fit. For nearly all the binary systems under consideration, the number of data points was enough to treat B_{12} as an independent parameter. In those cases where the number of data points is limited, the number of degrees of freedom (i.e., the number of parameters) must also be decreased. This can be done with the help of combination rules, which link the mixing B's and C's in some way to the B and C of the pure component.

A well-known combining rule for B_{12} is given by

$$B_{12} = \zeta_{12}(B_{11} B_{22})^{1/2} \tag{4}$$

Substituting Eq. (4) in Eq. (3a) reduces the number of parameters by two. Note that the temperature dependence of B_m is now determined by the temperature dependence of B_{11} and B_{22}. In many cases, $|\zeta_{12}|$ will be of the order 1. Problems arise when one of the pure components is around the Boyle temperature or even on the other side of it. In that case a better result may be obtained with

$$B_{12} = \zeta(B_{11} + B_{22}) \tag{5}$$

which has, incidentally, been applied in our work.

Because C_m depends on twice as many parameters, to be determined from binary mixtures, the drawback of insufficient data is even more serious. In case data are available for a single composition, a free-parameter fit easily results in very unreliable values for C_{112} and C_{122}; they can become an order of magnitude larger than expected and with the opposite sign. Clearly, in that case the mixing terms compensate mutually up to a great extent. An obvious mixing rule that can be used to constrain the results is, in analogy to Eq. (4),

$$c_{ijk} = \zeta_{ijk}(C_{iii}C_{jjj}C_{kkk})^{1/3}; \qquad i=j \text{ or } j=k \tag{6}$$

This relates the temperature dependence of the mixing C's to the C's of pure components. Nevertheless, this method can easily result in unrealistic values for ζ_{112} and ζ_{122}; for instance, $|\zeta| \gg 1$ but opposite in sign. To overcome this problem, one can oppose the condition

$$\zeta_{112} = \zeta_{122} \tag{7}$$

but it is to be expected that the fit for the compressibility factor will become less satisfactory. An even more serious consequence of this constraint may be that the values for the B's will also be affected, i.e., errors in C are compensated by introducing errors in B.

Recently, a new combination rule for third virial coefficients of mixtures has been proposed by McGregor et al. [2]. An attractive feature of this rule is that it is based on physical considerations of three-particle interactions:

$$C_{112} - C_{122} = \tfrac{1}{3}(C_{111} - C_{222}) \tag{8}$$

In those cases where we applied this rule, the final fit for the compressibility factor was as good as for a completely free nine-parameter fit. Moreover, it gave the same numbers for B_{12}.

The usefulness of the procedure mentioned above can be demonstrated by an example given in Table II. The numbers pertain to a mixture of CH_4 and CO. For this mixture, reliable results for the compressibility factor were available for only one single mixture (3% CO). The analysis was

Table II. Results for the Second and Third Cross Virial Coefficients for the Mixture CH_4–CO (for Methods See Text)

T(C)	$B_{12}(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$C_{112}(\mathrm{cm}^6 \cdot \mathrm{mol}^{-2})$	$C_{122}(\mathrm{cm}^6 \cdot \mathrm{mol}^{-2})$
		Method a: RMS dev $\approx 8 \times 10^{-5}$	
0	−31.2	−17,757	656,703
20	−26.3	−16,525	617,583
40	−20.0	−15,498	580,106
		Method b: RMS dev $\approx 1 \times 10^{-4}$	
0	−30.7	2,372	2,115
20	−24.9	2,208	1,989
40	−18.7	2,070	1,869
		Method c: RMS dev $\approx 8 \times 10^{-5}$	
0	−31.2	2,545	2,196
20	−26.3	2,496	2,277
40	−19.9	2,321	2,118

performed using three methods: (a) with free parameters; (b) using the relation $\xi_{112} = \xi_{122} = 1$; and (c) using Eq. (8)

Note that method c leads essentially to the same values for B and the same RMS deviation as method a, but method c gives sensible numbers for C_{112} and C_{122}. The constraint applied in method b is reflected in the increase in the RMS deviation.

Generally, very little is known about cross third virial coefficients. One of the few examples that can be found in the literature pertains to the mixture CH_4–N_2. In Table III, results for B_{12}, C_{112}, and C_{122} obtained from Ref. 1 are given in comparison with the results of our calculations for this mixture. From this table it can readily be seen that the results are in very good agreement, although this agreement is of modest meaning due to the large uncertainty limits in the published results.

Table III. Comparison of New Results for Cross Virial Coefficients for the Mixture CH_4–N_2 at 291.4 K with Published Data

	B_{12} $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	C_{112} $(\mathrm{cm}^6 \cdot \mathrm{mol}^{-2})$	C_{122} $(\mathrm{cm}^6 \cdot \mathrm{mol}^{-2})$
Dymond and Smith [1]	−20.1 ± 0.4	2100 ± 500	1600 ± 500
This work	−20.29	2054	1722

In our final work, which was concerned with natural gases, the third virial coefficients of some pure components were not available. Those components (heavy hydrocarbons) are present only at rather low concentrations, e.g., less than 1%. This does not turn out to be a problem, not only because C has a low value for these components but also, as can be seen from Eq. (3b), because their contributions are negligible since they are multiplied by the third power of the concentrations. Even the contribution of C_{122} can, in some cases, be neglected.

A final remark should be made about ternary coefficients. As noted in Section 1, for mixtures with more than two components the third virial coefficient C_{mix} also contains a ternary term: $x_1 x_2 x_3 C_{123}$. Experimental data for ternaries are scarce. In fact, one can calculate values for C_{123} to obtain the best fit for the compressibility, for instance, as we have done for the mixture CH_4–C_2H_6–C_3H_8. Nevertheless, one must be aware that the result for this term has a poor meaning in physical sense: it contains compensations for the shortcomings in the values for all the other terms! In those cases it is often better to assume $\xi_{ijk} = 1$ in Eq. (6).

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