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## ON SECOND VIRIAL COEFFICIENTS OF GASES AND GAS MIXTURES

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**Key Words:** Gas, Gas Mixture, Virial Equation, Second Virial Coefficient, Third Parameter

Molar refraction and molar polarization were used as new third parameters to correlate the second virial coefficients of nonpolar and polar gases, and their mixtures. A set of consistent data from the compilation of Dymond and Smith<sup>6)</sup> was used for the source data. The correlation was compared extensively with the correlations of Tsonopoulos, Tarakad-Danner, Brewer, Kubic and Vetere. In addition to the new third parameter, the utility of Pitzer's acentric factor was also tested. The correlation developed was of the general type

$$BPc/RTc = f^{(0)}(T/Tc) + \kappa \cdot f^{(1)}(T/Tc) \quad (1)$$

Where  $\kappa$  is the third parameter.

### Introduction

The non-ideal behavior of gases arising from intermolecular interactions in principle can be explained through the virial coefficients. The virial coefficients, either in pressure or reciprocal volume series, can be evaluated using potential energy functions such as the Lennard-Jones potential energy function.

The virial equation

$$Z = 1 + B'P + C'P^2 + \text{higher-order terms} \quad (2)$$

or

$$Z = 1 + B/V + C/V^2 + \text{higher-order terms} \quad (3)$$

is often truncated after the second term. There are several reasons for the use of  $B$  only. For example, (i)

experimental virial coefficients other than  $B$  are rarely available, and even if available are of very low accuracy; (ii) when the virial equation is used for moderate pressures, it is sufficient to use the second virial coefficients; (iii) the virial equation by its nature diverges at higher density and therefore its application is limited in spite of the theoretical background; and (iv) virial coefficients higher than the third with the non-additive contribution have not been evaluated for potential energy functions other than the Lennard-Jones potential function.

Pitzer<sup>14)</sup> did the first work on the generalization of second virial coefficients by introducing a third parameter, the acentric factor,  $\omega$ . Its applicability is limited to nonpolar and slightly polar compounds only. Also, experimental data of the vapor pressure at  $Tr=0.7$  is needed. Tsonopoulos<sup>18)</sup> modified Pitzer's equation for polar compounds. This correlation with nine to eleven constants can predict the second virial

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coefficients of some nonpolar and polar compounds. But its applicability is still limited. Tarakad and Danner<sup>17)</sup> introduced the radius of gyration as the third parameter instead of  $\omega$ , and developed a generalized equation based on Tsonopoulos' equation. The advantage of this parameter is that it can be obtained without experimental data. But the fourth parameter for polar compounds needs experimental data at  $Tr=0.6$ . Other workers, for example, Nothnagel,<sup>13)</sup> Stiel,<sup>10,11)</sup> Hayden and O'Connell<sup>7)</sup> have also contributed to the development of generalized equations. Both Stiel's and Hayden's equations use the Lennard-Jones potential function parameters. Nothnagel's equation was developed on the basis of a chemical theory, not the physical theory often used. These equations can predict second virial coefficients of nonpolar compounds like simple fluids and hydrocarbons successfully. Recently McCann and Danner<sup>12)</sup> proposed a correlation that uses the concept of group contributions to predict second virial coefficients. For polar compounds, however, no reliable correlation has been developed.

## 1. Present Work

### 1.1 Selection of data set

The data used in the present work were those compiled by Dymond and Smith.<sup>6)</sup> The compounds chosen cover a wide range of chemical nature, and particular attention was paid to compounds which are components of binary mixtures for which data are available. When several sets of data were available for each compound or the mixture, the data were chosen by the following criteria in the order enumerated:

1. The smoothed data set recommended by the authors was used.

2. When a smoothed data set was not available or recommended, and multiple data sets were available, the best data based on the ratings were chosen. The ratings given are  $\pm 2\%$  or  $1.0 \text{ cm}^3/\text{mol}$  as class I,  $\pm 10\%$  or  $15 \text{ cm}^3/\text{mol}$  as class II and more than  $10\%$  or  $15 \text{ cm}^3/\text{mol}$  as class III.

3. When the data sets were of the same ratings, then the set which covered the maximum temperature range was chosen.

Many data for nonpolar compounds, especially hydrocarbons, exist in the literature compared to all other classes of compounds. It is therefore important to see that a large number of hydrocarbon data is not used in developing and testing correlations, as this would produce a biased conclusion. This situation was avoided by choosing data for a few hydrocarbons and some other nonpolar compounds to develop the correlation, and reserving the other hydrocarbon and nonpolar compound data to test the correlation. Reduced second virial coefficients for these compounds were plotted against reduced temperature,

and data for the correlation were read at uniform  $Tr$  intervals. Reduced temperatures up to 2.0 were covered and this method of obtaining the data set avoided too great a deviation in the distribution of data points.

For polar compounds and binary mixtures, the data sets given in a reference<sup>6)</sup> were used.

### 1.2 Selection of correlation parameters

The parameters used in the present work are the critical properties ( $T_c$ ,  $P_c$ ,  $V_c$ ), the acentric factor ( $\omega$ ), the molar refraction ( $Rm$ ) and the dipole moment ( $\mu$ ). All the values except those of  $Rm$  were taken from Reid and coworkers.<sup>16)</sup> The  $Rm$  values were calculated on the basis of the group contribution method.<sup>1,2)</sup> For polar compounds, the dipole moment was used in the form of molar polarization defined as

$$Pm = Rm + 4\pi N\mu^2/(9kT) \quad (4)$$

or

$$Pmc = Rm + 4\pi N\mu^2/(9kT_c) \quad (5)$$

Besides using  $Pm$  (or  $Pmc$ ),  $Rm$  and  $\mu$  as  $4\pi N\mu^2/(9kT)$  (or  $4\pi N\mu^2/(9kT_c)$ ) were used as distinct parts in the correlations. The second virial coefficient of polar compounds,  $B_{\text{polar}}$ , was then expressed as

$$B_{\text{polar}} = B_{\text{nonpolar}} + \text{correction term} \quad (6)$$

To correlate  $B_{12}$  of mixtures, the following mixing rules were used.

$$\omega_{12} = (\omega_1 + \omega_2)/2 \quad (7)$$

$$Rm_{12} = [(Rm_1^{1/3} + Rm_2^{1/3})/2]^3 \quad (8)$$

$$Vc_{12} = [(Vc_1^{1/3} + Vc_2^{1/3})/2]^3 \quad (9)$$

$$Tc_{12} = (Tc_1 \cdot Tc_2)^{1/2} \quad (10)$$

$$Pc_{12} = [(Pc_1^{2/3} + Pc_2^{2/3})/2]^{3/2} \quad (11)$$

Equation (11) is not the common mixing rule used by other authors. Generally,  $Pc_{12}$  is used as

$$Pc_{12} = 4Tc_{12}(Pc_1 Vc_1/Tc_1 + Pc_2 Vc_2/Tc_2)/(Vc_1^{1/3} + Vc_2^{1/3})^3 \quad (12)$$

and  $Tc_{12}$  as

$$Tc_{12} = (Tc_1 \cdot Tc_2)^{1/2}(1 - k_{12}) \quad (13)$$

The advantages of Eqs. (10) and (11) are that the interaction parameter  $k_{12}$  and the critical volume are eliminated. It was found that when the new rule for  $Pc_{12}$  given by Eq. (11) was used with the geometric mean for  $Tc_{12}$ , results as good as those by Eqs. (12) and (13) were obtained.

### 1.3 Computation using SAS

The correlation for the second virial coefficient in general was carried out by use of the relation

$$B Pc / RTc = f^{(0)}(Tr) + f^{(1)}(Tr, A) \quad (14)$$

where  $A$  is a third parameter.

In this study two SAS procedures, PROC RSQUARE and PROC GLM, were used.<sup>15)</sup>

As the criterion for choosing the best combination of independent variables, the  $R^2$  value was used. PROC RSQUARE can evaluate all possible combinations and give  $R^2$ .

The  $R^2$  value is defined by

$$\sum (Y_i - \bar{Y})^2 = \sum (\hat{Y}_i - \bar{Y})^2 + \sum (Y_i - \hat{Y}_i)^2 \quad (15)$$

$$R^2 = \sum (\hat{Y}_i - \bar{Y})^2 / \sum (Y_i - \bar{Y})^2 \quad (16)$$

where  $Y_i$  is the data value,  $\hat{Y}_i$  the predicted value and  $\bar{Y}$  the mean value.

For comparison with other available equations, the average absolute deviation (Avg), the bias (Bias), the root mean square deviation (RMS) and the absolute percentage deviation (Dev) were calculated as follows.

$$\text{Avg} = \sum |B_{\text{calc}} - B_{\text{expt}}| / n \quad (\text{cc/mol}) \quad (17)$$

$$\text{Bias} = \sum (B_{\text{calc}} - B_{\text{expt}}) / n \quad (\text{cc/mol}) \quad (18)$$

$$\text{RMS} = \sqrt{\sum (B_{\text{calc}} - B_{\text{expt}})^2 / n} \quad (\text{cc/mol}) \quad (19)$$

$$\text{Dev} = \sum |100(B_{\text{calc}} - B_{\text{expt}}) / B_{\text{expt}}| / n \quad (\%) \quad (20)$$

$n$  is the number of points.

## 2. Results and Discussion

The data sets were divided into five classes: 1, pure nonpolar gases; 2, pure polar gases; 3, nonpolar-nonpolar mixtures; 4, nonpolar-polar mixtures; and 5, polar-polar mixtures.

### 2.1 Nonpolar compounds

Table 1 shows the different functional forms used to fit the data. The third parameters used in the correlations were selected from  $Rm$ ,  $\omega$ ,  $Vc$  and  $Vc_i = RTc/Pc$  (pseudo-critical volume).

Overall, it was found that seven constants reproduced the experimental data within the limits of experimental accuracy, and that increasing the number of constants was not useful.

The choice of independent variables was made on the basis of the  $R^2$  value. The best combination of variables changed slightly with the parameters used in the model equations. The following equations are proposed for correlating second virial coefficients of nonpolar substances:

$$BPC/RTc = f^{(0)} + \kappa \cdot f^{(1)} \quad (21)$$

$$f^{(0)} = a_0 + a_1/Tr + a_2/Tr^2 + a_5/Tr^5 \quad (22)$$

$$f^{(1)} = b_0 + b_5/Tr^5 + b_6/Tr^6 \quad (23)$$

$\kappa = Rm$

$$a_0 = 0.13840496 \quad a_1 = -0.29251393$$

$$a_2 = -0.17620889 \quad a_5 = 0.00606184$$

Table 1. Examples of model equations tested using SAS

$$\begin{aligned} Y &= \sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i) \\ Y &= \sum (a_{ij}/X^i) + VI \cdot \sum (b_{ij}/X^i) \\ Y &= \sum (a_{ij}/X^i) + PP \cdot \sum (b_{ij}/X^i) \\ Y &= \sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i) + KK \cdot \sum (c_{ij}/X^i) \\ BV &= \sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i) \\ BV &= \sum (a_{ij}/X^i) + PP \cdot \sum (b_{ij}/X^i) \\ BV &= \sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i) + KK \cdot \sum (c_{ij}/X^i) \\ SA &= \kappa \cdot \sum (a_{ij}/X^i) \\ SA &= PP \cdot \sum (a_{ij}/X^i) \\ SA &= KK \cdot \sum (a_{ij}/X^i) \\ Y &= \exp[\sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i)] \\ Y &= \exp[\sum (a_{ij}/X^i) + PP \cdot \sum (b_{ij}/X^i)] \\ Y &= \exp[\sum (a_{ij}/X^i) + \kappa \cdot \sum (b_{ij}/X^i) + KK \cdot \sum (c_{ij}/X^i)] \\ Y &= a + b/X + c \cdot \kappa \cdot \exp(dX) \\ Y &= a + b/X + c \cdot \exp(d \cdot \kappa \cdot X) \\ Y &= a \cdot \exp(bX) + c \cdot \kappa \cdot \exp(dX) \\ Y &= a + b/X^m + c \cdot \kappa \cdot X^n \quad \text{etc.} \end{aligned}$$

Notation for this table:

$$\begin{aligned} Y &= BPC/RTc \\ BV &= B/Vc \\ X &= T/Tc \\ \kappa &= Rm, \omega \text{ or } Vc \\ VI &= Vc_i \\ PP &= Pm \text{ or } Pmc \\ KK &= 4\pi N\mu^2/(9kT) \text{ or } 4\pi N\mu^2/(9kTc) \\ SA &= [BPC/RTc]_{\text{polar}} - [BPC/RTc]_{\text{nonpolar}} \\ N &= \text{Avogadro constant} \\ k &= \text{Boltzmann constant} \\ a, b, c, d, m \text{ and } n &\text{ are constants} \end{aligned}$$

$$b_0 = 0.00065856 \quad b_5 = -0.00185336$$

$$b_6 = 0.00020621$$

$\kappa = \omega$

$$a_0 = 0.14327939 \quad a_1 = -0.30882559$$

$$a_2 = -0.15627133 \quad a_5 = -0.00645476$$

$$b_0 = 0.05499040 \quad b_5 = -0.15064221$$

$$b_6 = 0.01979980$$

$\kappa = Vc$

$$a_0 = 0.14384416 \quad a_1 = -0.31488091$$

$$a_2 = -0.16330383 \quad a_5 = 0.00933272$$

$$b_0 = 0.00007034 \quad b_5 = -0.00016253$$

$$b_6 = 0.00001534$$

From Table 2, it can be seen that, overall, Brewer's equation<sup>3)</sup> gives large errors due to too few constants and lack of a third parameter. Tsonopoulos' equation shows lower deviations but contains nine constants. Kubic's equation<sup>9)</sup> has different values of constants from Tsonopoulos' but the form of equation and the parameters are identical. Tarakad-Danner's equation produced less RMS compared to Tsonopoulos' equation since more constants are added. The present calculations show that the use of the acentric factor produces lower RMS, but Dev for  $\omega$ ,  $Rm$  and  $Vc$  are

**Table 2.** Overall comparison of proposed equations with other equations

Data <sup>a</sup> set	Eqn. <sup>b</sup>	# Const.	# Data <sup>c</sup> points	Avg [cm <sup>3</sup> /mol]	Bias [cm <sup>3</sup> /mol]	RMS [cm <sup>3</sup> /mol]	Dev. [%]
NP	<i>B</i>	3	185 (19)	62.7	-57.3	182.9	13.7
NP	<i>T</i>	9	185 (19)	10.0	1.7	31.6	4.7
NP	<i>K</i>	9	185 (19)	12.6	-5.5	32.2	6.2
NP	<i>TD</i>	10-11	185 (19)	9.7	-2.6	17.7	6.5
NP	<i>Rm</i>	7	185 (19)	15.6	0.9	56.5	5.8
NP	$\omega$	7	185 (19)	10.5	0.9	31.3	4.5
NP	<i>Vc</i>	7	185 (19)	15.4	0.2	53.8	5.5
P	<i>T</i>	10-11	171 (24)	56.8	21.0	121.3	8.0
P	<i>TD</i>	10-11	278 (35)	46.8	-2.1	90.8	8.1
P	<i>V</i>	14	301 (38) <sup>d</sup>	91.7	-25.1	141.5	14.3
P	<i>Rm</i>	9	327 (40)	16.0	0	31.0	3.3
NP-NP	<i>T</i>	9	356 (32)	7.7	-0.6	15.7	21.9
NP-NP	<i>TD</i>	10-11	548 (55)	15.6	3.1	69.6	37.9
NP-NP	<i>Rm</i>	7	478 (50)	21.9	-2.1	79.9	38.9
NP-NP	$\omega$	7	590 (60)	18.1	-3.6	66.5	39.7
NP-NP	<i>Vc</i>	7	590 (60)	18.7	-2.0	73.6	42.5
NP-P	<i>T</i>	9	119 (24)	25.4	0.2	65.0	7.8
NP-P	<i>TD</i>	10-11	177 (33)	32.2	9.9	65.2	16.6
NP-P	<i>Rm</i>	7	177 (33)	44.4	-29.1	74.2	32.4
NP-P	$\omega$	7	177 (33)	54.0	-40.9	100.2	35.8
NP-P	<i>Vc</i>	7	177 (33)	41.2	-23.3	67.6	32.4
P-P	<i>T</i>	10-11	52 (11)	33.4	-1.5	47.1	6.8
P-P	<i>TD</i>	10-11	83 (20)	250.8	229.3	375.9	24.6
P-P	<i>Rm</i>	9	88 (22)	222.3	147.4	335.7	21.7

Note:

<sup>a</sup> NP, nonpolar compound data set; P, polar compound data set; NP-NP, nonpolar-nonpolar mixture data set; NP-P, nonpolar-polar mixture data set; P-P, polar-polar mixture data set.

<sup>b</sup> *B*, Brewer's equation; *T*, Tsonopoulos' equation; *K*, Kubic's equation; *V*, Vetere's equation; *TD*, Tarakad-Danner's equation; *Rm*, proposed *Rm* equation;  $\omega$ , proposed  $\omega$  equation; *Vc*, proposed *Vc* equation.

<sup>c</sup> The numbers in parentheses denote the number of compounds.

<sup>d</sup> Water and ammonia are eliminated.

very close to one another.

## 2.2 Polar compounds

Polar compounds need a parameter to characterize their polarity. Tarakad and Danner used a characterizing parameter  $\Phi$  which is substance-dependent. They assume that the polar effects are negligible if  $\Phi=0$ . According to this, a nonpolar compound sometimes becomes polar and vice versa. Such inconsistencies are avoided in the present work. Tsonopoulos' equation involves constants based on homologous groups. The number of homologous groups considered by the author is limited.

Based on the success of earlier work on compressibility correlations,<sup>19)</sup> the molar polarization (*Pm* or *Pmc*) was used as the polarity characterizing parameter. In this study, the second term of *Pm* was introduced independently to characterize the polarity. The equation form used here is

$$BPc/RTc = f^{(0)} + Rm \cdot f^{(1)} + f^{(2)} \quad (24)$$

$f^{(0)}$  and  $f^{(1)}$  are given by Eqs. (22) and (23)

and

$$f^{(2)} = p + q \cdot [4\pi N\mu^2 / (9kT)] / Tr^5 \quad (25)$$

where *p* and *q* are constants for the polarity terms. A total regression analysis similar to that carried out for nonpolar compounds gave 259.1 cm<sup>3</sup>/mol RMS and 17.5% Dev. These deviations are greater than the experimental error. Therefore, *p* and *q* were obtained through independent regressions which are shown in **Table 3**. The compounds selected for this data set had a dipole moment greater than unity.

Vetere's equation<sup>16)</sup> can be eliminated from discussion as it gives large RMS and Dev with as many as 14 constants. Tsonopoulos' result also shows large RMS. Dev calculated using Tarakad-Danner's correlation was 8.1%, but RMS was 91 cm<sup>3</sup>/mol compared to a value of 121 cm<sup>3</sup>/mol for Tsonopoulos' correlation.

The overall comparison for polar compounds shown in Table 2 reveals that the proposed *Rm* equation with nine constants for 40 substances (327

**Table 3.** Constants for polar compounds in proposed  $R_m$  equation\*

Compound	# Data points	$p \times 10^2$	$q \times 10^3$	$R^2$
CHCl <sub>3</sub>	5	-0.3833	-0.163	0.8075
CH <sub>3</sub> Cl	10	0.2845	-0.290	0.8644
NH <sub>3</sub>	8	-0.0424	-1.280	0.9953
SO <sub>2</sub>	16	-1.2539	-0.636	0.9758
CH <sub>3</sub> CN	5	8.0904	-1.058	0.9924
CH <sub>3</sub> OH	6	-1.6545	-2.736	0.9655
C <sub>2</sub> H <sub>5</sub> OH	10	97.7804	-6.536	0.9533
N-CH <sub>3</sub> H <sub>7</sub> OH	4	8.4798	-1.373	0.9810
2-C <sub>3</sub> H <sub>7</sub> OH	4	16.5138	-2.192	0.9733
N-C <sub>4</sub> H <sub>9</sub> OH	7	17.5924	-1.249	0.8974
iso-C <sub>4</sub> H <sub>9</sub> OH	4	17.4438	-1.787	0.9524
sec-C <sub>4</sub> H <sub>9</sub> OH	4	16.7624	-1.728	0.9890
tert-C <sub>4</sub> H <sub>9</sub> OH	4	22.7179	-2.221	0.9729
MeOMe	3	-2.3198	-0.843	0.9989
EtOEt	7	12.6833	-0.853	0.9968
(iso-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> O	3	-3.4899	-0.001	0.0001**
HCOOMe	11	-3.3137	-0.712	0.9840
CH <sub>3</sub> COOMe	13	-8.8894	-0.715	0.9157
CH <sub>3</sub> CHO	12	-3.1601	-0.813	0.9830
C <sub>2</sub> H <sub>5</sub> CHO	4	9.0500	-0.599	0.9906
MeCOMe	10	2.1690	-0.478	0.9988
MeCOEt	5	-5.7366	-0.194	0.9626
iso-C <sub>3</sub> H <sub>7</sub> COMe	3	-10.8558	-0.152	0.9873
n-C <sub>3</sub> H <sub>7</sub> COMe	5	19.9710	-0.703	0.9739
EtCOEt	3	0.0007	-0.325	1.0000
MeNH <sub>2</sub>	12	-4.1109	-0.978	0.9976
EtNH <sub>2</sub>	11	-5.9308	-0.897	0.9553
(Me) <sub>3</sub> N	9	-0.6090	-0.844	0.6403
(Et) <sub>2</sub> NH	11	-4.9546	-0.254	0.5611
(Et) <sub>3</sub> N	12	2.2261	1.158	0.9151
CH <sub>3</sub> COOEt	17	-1.2918	-0.440	0.8770
HCOOCH <sub>2</sub> CH <sub>3</sub>	18	1.9706	-0.344	0.9207
CH <sub>2</sub> Cl <sub>2</sub>	5	3.3198	-0.096	0.7696
CH <sub>3</sub> Br	5	-24.5859	-0.269	0.8795
CH <sub>3</sub> I	4	18.0361	-0.115	0.8031
C <sub>2</sub> H <sub>5</sub> Cl	16	4.8307	-0.357	0.9858
C <sub>2</sub> H <sub>5</sub> Br	2	2.7414	0.002	1.0000
n-C <sub>3</sub> H <sub>7</sub> Cl	17	3.9854	-0.065	0.9108
tert-C <sub>4</sub> H <sub>9</sub> Cl	4	-9.1691	0.269	0.9970
H <sub>2</sub> O	18	6.9027	-1.834	0.9255

Note:

\*  $SA = [BPC/RTc]_{\text{polar}} - [BPC/RTc]_{\text{nonpolar}} = \text{Eq. (25)}$ .

Regressions have been made for each compound.

\*\*  $R^2$  value of (iso-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>O is considerably low due to very small  $SA$ .

data points) gives 3.3% deviation and 31.0 cm<sup>3</sup>/mol RMS by independent regression analysis.

### 2.3 Nonpolar-nonpolar mixtures

The  $B_{12}$  values were predicted by use of the nonpolar pure substance equation and the mixing rules shown earlier.

A comparison among the different correlations was made for 60 mixtures comprising 590 data points. The results are shown in Table 2. However, for lack of required data, Tsonopoulos' equation could be compared for only 32 mixtures and 356 points, Tarakad-Danner's equation for 55 mixtures and 548 points and

the present equations with  $R_m$  for 50 mixtures and 478 points, and with  $\omega$  and  $V_c$  for 60 mixtures and 590 points. Tsonopoulos used  $k_{12}$  values from References 4, 5 and 8.

To understand the performance of each correlation, data matching was done. The results based on RMS and Dev are shown in Table 4, from which it is seen that the proposed equations with  $R_m$  and  $V_c$  work with about the same accuracy and  $\omega$  gives slightly better results. For 356 points, Tsonopoulos' equation gives the smallest deviations. For more points, the deviations of Tarakad-Danner's correlation are almost the same as those of the proposed equations.

### 2.4 Nonpolar-polar mixtures

In this class the nonpolar compounds have exactly zero dipole moment and those of polar compounds are greater than zero. In the case of nonpolar-polar mixtures, it was assumed that the polar effects are negligible, based on the correlations of Tsonopoulos and Tarakad-Danner. The correlations except for Tsonopoulos' correlation were applied to 33 compounds and 177 points. A summary of the results is shown in Table 2.

In Table 5 the results of data matching based on RMS and Dev are shown. They show that Tsonopoulos' and Tarakad-Danner's correlations give smaller errors than the proposed correlations due to the use of  $k_{12}$ . The proposed  $\omega$  equation produced larger deviations, especially in RMS, than the other proposed equations, which is contrary to the case of nonpolar-nonpolar mixtures.

### 2.5 Polar-polar mixtures

Available data for this class of compounds are for fewer than for other classes. Also, the data are less accurate. For these mixtures a strong long-range interaction force exists, especially when the dipole moments of both polar compounds are greater than unity.

Tsonopoulos' and Tarakad-Danner's equations use  $k_{12}$  besides the suggested mixing rules for each mixture. As noted in their papers,  $k_{12}$  was obtained by use of experimental data. Thus without  $k_{12}$  the results become poorer. In addition, Tarakad and Danner do not use their own mixing rule for  $\Phi$  as it leads to large deviations.

$B_{12}$  values were predicted in the present work by using the polar pure substance correlation, the mixing rules used for nonpolar-nonpolar mixtures and the following mixing rules for polarity terms.

$$p_{12} = (p_1 + p_2)/2 \quad (26)$$

$$q_{12} = (q_1 + q_2)/2 \quad (27)$$

$$\mu_{12} = (\mu_1 + \mu_2)/2 \quad (28)$$

Substances with  $\mu < 1$  were treated as  $p = 0$  and

**Table 4.** Comparison of nonpolar-nonpolar mixtures by data matching

Equation	$T$	$TD$	$Rm$	$\omega$	$Vc$
Parameter	$Tc\ Pc$ $\omega\ k_{12}$	$Tc\ Pc$ $RG\ \Phi\ k_{12}$	$Tc\ Pc$ $Rm$	$Tc\ Pc$ $\omega$	$Tc\ Pc$ $Vc$
# Const.	9	10–11	7	7	7
# Points	356	356	307*	356	356
RMS	15.7	16.2	19.9	19.5	19.0
Dev.	21.9	34.8	41.2	36.3	40.0
# Points	—	436**	478	478	478
PMS	—	83.2	79.9	73.8	81.7
Dev.	—	38.7	38.9	35.7	40.0
# Points	—	548	—	548	548
RMS	—	69.6	—	68.5	75.9
Dev.	—	37.9	—	39.6	42.5
# Points	—	—	—	590	590
RMS	—	—	—	66.5	73.6
Dev.	—	—	—	39.7	42.5

Note:

\* Ar+He, Ar+Ne, He+Ne, He+N<sub>2</sub> and H<sub>2</sub>+He are not included.

\*\* Ar+SF<sub>6</sub>, SF<sub>6</sub>+Kr, CF<sub>4</sub>+SF<sub>6</sub>, CH<sub>4</sub>+SF<sub>6</sub> and neo-C<sub>5</sub>H<sub>12</sub>+SF<sub>6</sub> are not included.

**Table 5.** Comparison of nonpolar-polar mixtures by data matching

Equation	$T$	$TD$	$Rm$	$\omega$	$Vc$
Parameter	$Tc\ Pc$ $\omega\ K_{12}$	$Tc\ Pc$ $RG\ \Phi\ k_{12}$	$Tc\ Pc$ $Rm$	$Tc\ Pc$ $\omega$	$Tc\ Pc$ $Vc$
# Const.	9	10–11	7	7	7
# Points	119	119	119	119	119
PMS	65.0	67.7	85.3	117.2	75.9
Dev.	7.8	12.6	30.9	36.2	30.3
# Points	—	177	177	177	177
PMS	—	65.2	74.2	100.2	67.6
Dev.	—	16.6	32.4	35.8	32.4

$q=0$ .

To compare the performance of these three equations, the results of data matching are shown in **Table 6** and a summary in Table 2. Tsonopoulos' equation gives better results for 52 points, but the availability of parameters is limited. Though Tarakad-Danner's correlation has more constants than the proposed  $Rm$  equation, its deviations are almost the same. Also, the parameters in Tarakad-Danner's equation are not readily available. The proposed equation has no  $k_{12}$ .

From this discussion, it can be said that if each term in the molar polarization is used separately, the  $B_{12}$  value for polar-polar mixtures can be predicted by use of the proposed  $Rm$  equation with the same error as

**Table 6.** Comparison of polar-polar mixtures by data matching

Equation	$T$	$TD$	$Rm$
Parameter	$Tc\ Pc\ \omega\ k_{12}$ $\mu\ a\ b$	$Tc\ Pc\ k_{12}$ $RG\ \Phi$	$Tc\ Pc\ Rm\ \mu$ $p\ q$
# Const.	10–11	10–11	9
# Points	52	49*	52
RMS	47.1	82.8	112.3
Dev.	6.8	14.1	13.6
# Points	—	83	83
RMS	—	375.9	344.6
Dev.	—	24.6	22.3

Note:

\* C<sub>2</sub>H<sub>5</sub>Cl+C<sub>3</sub>H<sub>7</sub>Cl is not included.

Tarakad-Danner's equation.

## Conclusion

In the case of nonpolar compounds, third parameters like  $Rm$ ,  $\omega$  and  $Vc$  can be used successfully to correlate second virial coefficients. The proposed correlations contain seven empirical constants, fewer than other correlations. The average absolute deviation (Dev) was 5–6% and the root mean square deviation (RMS) 30–60 cm<sup>3</sup>/mol.

A fourth parameter is required to treat polar compounds. The substance-dependent correlation yielded good results with Dev of 3% and RMS of 31 cm<sup>3</sup>/mol for 40 compounds, 327 points. However, no correlation could be obtained among the substance-dependent parameters  $p$  and  $q$ . Polar effects are greater for  $Tr \leq 1$ , decreasing with increase in temperature.

For nonpolar-nonpolar mixtures the results of the proposed equations without  $k_{12}$  are comparable to Tarakad-Danner's equation. Dev was 39–43% and RMS 67–80 cm<sup>3</sup>/mol. For nonpolar-polar mixtures the deviations of the proposed equation were slightly higher than in the correlations of Tsonopoulos and Tarakad-Danner, as shown in Tables 2 and 5. Dev was 32–36% and RMS 68–100 cm<sup>3</sup>/mol. For 22 polar-polar mixtures a total of 88 points were compared. Dev was 23% and RMS 386 cm<sup>3</sup>/mol. The results shown in Tables 2 and 6 indicate that the Tsonopoulos correlation seems to be the best. However, the lack of necessary parameters in that correlation restricts its applicability. The proposed correlation with nine constants performed better than Tarakad-Danner's correlation.

Finally, it can be stated that by overall comparison the proposed equations with fewer constants predict  $B$  or  $B_{12}$  values with similar or better accuracy than other correlations. The use of  $Rm$  as a correlating

parameter eliminates the need for experimental vapor pressure data to calculate  $\omega$ . Elimination of the interaction parameter,  $k_{12}$ , makes this correlation easier to use. Detailed tables of source data and comparison of results are available from the authors.

#### Nomenclature

$B$	= second virial coefficient	[cm <sup>3</sup> /mol]
$B'$	= second virial coefficient	[Pa]
$B_{12}$	= interaction second virial coefficient	[cm <sup>3</sup> /mol]
$C$	= third virial coefficient	[(cm <sup>3</sup> /mol) <sup>2</sup> ]
$C'$	= third virial coefficient	[Pa <sup>-2</sup> ]
$k$	= Boltzmann constant	[J/K]
$k_{12}$	= interaction parameter in the mixture	
$N$	= Avogadro constant	[molecules/mol]
$P$	= pressure	[Pa]
$P_c$	= critical pressure	[Pa]
$P_m, P_{mc}$	= molar polarization	[cm <sup>3</sup> /mol]
$p$	= polar term constant in the proposed equation	[mol/cm <sup>3</sup> ]
$q$	= polar term constant in the proposed equation	[mol/cm <sup>3</sup> ]
$R$	= universal gas constant	[Pa · cm <sup>3</sup> /mol · K]
$R_m$	= molar refraction	[cm <sup>3</sup> /mol]
$RG$	= radius of gyration	[nm]
$T$	= temperature	[K]
$T_c$	= critical temperature	[K]
$T_r$	= reduced temperature	
$V$	= volume	[cm <sup>3</sup> /mol]
$V_c$	= critical volume	[cm <sup>3</sup> /mol]
$V_{c_i}$	= pseudo-critical volume = $RT_c/P_c$	[cm <sup>3</sup> /mol]
$X_i$	= mole fraction of component $i$	[—]
$Z$	= compressibility factor	[—]
$Z_c$	= critical compressibility factor	[—]
$\kappa$	= parameter $R_m$ , $\omega$ or $V_c$	[appropriate units]
$\mu$	= dipole moment	[Debye]
$\Phi$	= fourth parameter defined by Tarakad and Danner	

$\chi$	= Stiel polar factor
$\omega$	= acentric factor

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