Correlation for the Third Virial Coefficient Using T_c, P_c and ω As Parameters

An empirical correlation for the third virial coefficient of nonpolar gases is developed. The correlation requires a knowledge of the critical temperature, critical pressure and acentric factor of the compounds for the prediction of third virial coefficients in the absence of experimental data. The use of the correlation for mixtures of nonpolar gases, including quantum gases, requires one binary parameter for each binary interaction. Predictions are in good agreement with reported experimental data and with the values obtained with existing correlations.

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SCOPE

The pressure explicit virial equation of state, truncated after the second virial coefficient, is a useful expression for the calculation of thermodynamic properties of gases at conditions such that the reduced volume is greater than 2. According to recent studies (De Santis and Grande, 1979), the addition of the third virial coefficient extends the applicability of the virial equation to conditions of temperature and pressure for which the reduced volume is greater than 1.3.

Empirical correlations for the third virial coefficient (Chueh and Prausnitz, 1967a; Pope et al., 1973; De Santis and Grande, 1979) are either of limited applicability or require extensive information to characterize the compound.

This work presents a generalized correlation for the third virial coefficient of pure and mixed nonpolar compounds, including quantum gases, using critical temperature, critical pressure and acentric factor, similar to the successful empirical correlations for second virial coefficient (Pitzer and Curl, 1957; Tsonopoulos, 1974, 1979).

CONCLUSIONS AND SIGNIFICANCE

Third virial coefficients for nonpolar gases, including quantum gases, have been correlated using three characteristic parameters for each compound. These three parameters are the same required by successful correlations for the second virial coefficient, i.e., the critical temperature, the critical pressure and the acentric factor. This fact allows the use of the virial equation up to densities of the order of 0.75 the critical density using the same information that previously did not allow one to go beyond 0.5 the critical density. Third virial coefficients of mixtures of nonpolar gases, including quantum gases, may be predicted using one binary interaction parameter. Within the accuracy of the experimental information on the third virial coefficients, the new correlation performs as well as the more complex expressions existing in the literature.

The pressure explicit virial equation of state may be written as

$$P = \frac{RT}{v}\left(1 + \frac{B}{v} + \frac{C}{v^2} + \dots\right) \quad (1)$$

where B is the second virial coefficient, C is the third virial coefficient, etc. The virial coefficients are only a function of temperature for a given compound. In principle, they may be obtained from potential functions for intermolecular interactions.

In macroscopic terms, following the three parameter corresponding states theorem, nonpolar fluids may be characterized by the critical volume, the critical temperature and the acentric factor. Due to uncertainties or even unavailability of critical volume information, the critical pressure has been used instead in many correlations and equations of state. In fact, generalized correlations for second virial coefficients available in the literature (Pitzer and Curl, 1957; Tsonopoulos, 1974, 1979; Hayden and O'Connell, 1975; Tarakad and Danner, 1977) include the critical pressure instead of the critical volume in the set of characteristic parameters.

Correlations for the third virial coefficient presented in the literature (Chueh and Prausnitz, 1967a; Pope et al., 1973; De Santis and Grande, 1979), have used the critical volume as a parameter. This fact makes the use of the truncated virial equation awkward. Different pieces of information will be required whether the equation is truncated after the second or after the third virial coefficients. In addition to this common drawback, each of the existing correlations for third virial coefficients have other limitations that are discussed subsequently. The correlation of Chueh and Prausnitz (1967a) uses a parameter that can only be evaluated if there are some polarizability or third virial coefficient data available for the compound in question. The correlation of Pope et al. (1973) can only be used for compounds with an acentric factor not exceeding 0.1. The correlation of De Santis and Grande (1979) is the only one that has general predictive ability. However, it requires a knowledge of the dipole polarizability of the molecule and of Bondi's molecular volume (Bondi, 1968), in addition to the critical volume, critical temperature and acentric factor of the compound.

The correlation for the third virial coefficient presented in this work uses only three characteristic parameters for pure compounds: critical pressure, critical temperature and acentric factor. The desirability of having a correlation of this type has been previously discussed by Abbott (1973). For mixtures, one binary parameter per pair of compounds is required. These binary parameters are the same previously evaluated by Chueh and Prausnitz (1967b) using second virial coefficient data. Predictions of third virial coefficients by this correlation are in good agreement with the limited experimental information available and with the values obtained with the more complex correlation of De Santis and Grande.

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TABLE 1. SOURCES OF EXPERIMENTAL THIRD VIRIAL COEFFICIENTS

Argon	Michels et al. (1949), Michels et al. (1958), Crain and Sontag (1966), Levelt Sengers et al. (1972), Pope et al. (1973)
Krypton	Beattie et al. (1952), Whalley and Schneider (1954), Levelt Sengers et al. (1972)
Xenon	Beattie et al. (1951), Michels et al. (1954), Whalley et al. (1955), Levelt Sengers et al. (1972)
Nitrogen	Michels et al. (1934), Canfield et al. (1963), Hoover et al. (1964), Levelt Sengers et al. (1972)
Oxygen	Holborn et al. (1925) Michels et al. (1954), Levelt Sengers et al. (1972)
Carbon dioxide	Michels et al. (1935), MacCormack and Schneider (1950), Pfefferle et al. (1956), Butcher and Dadson (1964), Vukalovic and Masalov (1966), Levelt Sengers et al. (1972)
Methane	Michels et al. (1935), Michels et al. (1936), Schamp et al. (1958), Douslin et al. (1967), Hoover et al. (1968), Levelt Sengers et al. (1972)
Ethylene	Michels and Geldermans (1942), Butcher and Dadson (1964)
Ethane	Reamer et al. (1944), Michels et al. (1954), Pope et al. (1973)
Propylene	Michels et al. (1953), Waronwny et al. (1978)
Propane	Waronwny et al. (1978)
i-Butane	Connolly (1962)
n-Butane	Connolly (1962)
Neopentane	Beattie et al. (1952), Perez Masia et al. (1964), McKetta et al. (1967)
Benzene	Connolly and Kandalic (1960)
Octane	Connolly and Kandalic (1960)
Cyclohexane	Kerns et al. (1974)

CONSTRUCTION OF THE GENERALIZED EMPIRICAL CORRELATION

Experimental information on third virial coefficients is scarce and the discrepancy between reported values for the same compound is, in most cases, considerable. The sources of data used in this work are presented in Table 1.

Observation of the data of third virial coefficients plotted versus reduced temperature for different fluids by Chueh and Prausnitz (1967a), suggested that the curves for different compounds will almost coincide if the values of the third virial coefficients for each compound were divided by the value of the third virial coefficient of the same compound at its critical temperature, C_c.

In addition, it was found that the third virial coefficient at the critical temperature of each fluid, reduced using critical temperature and critical pressure as parameters, could be well correlated as a function of the acentric factor. This correlation is illustrated in Figure 1. In analytical terms, a regression analysis of the data depicted in Figure 1 indicated that the correlation may be expressed by

$$\frac{C_cP_c^2}{(RT_c)^2} = 0.03526 + 0.02566\,\omega \qquad (2)$$

From the above two observations, the generalized correlation for the third virial coefficients may be written as

$$\frac{CP_c^2}{(RT_c)^2} = \frac{C_cP_c^2}{(RT_c)^2}F^{(0)}_{(T_r)} + F^{(1)}_{(T_r,\omega)} \qquad (3)$$

where, by the conditions imposed, at the critical temperature the functions $F^{(0)}$ and $F^{(1)}$ take the values 1 and 0, respectively. While $F^{(0)}$ is assumed to be independent of the acentric factor, $F^{(1)}$ depends on both the reduced temperature and the acentric factor and must be zero at the critical temperature, irrespective of the value of the acentric factor.

The main function of temperature, $F^{(0)}$ was evaluated using data of compounds with acentric factor close to zero. Argon and Krypton were considered. Preliminary calculations showed that at high reduced temperatures it was not possible to fit both sets of data well. Krypton data was finally selected in the high reduced temperature range since it generated a function $F^{(0)}$ that allowed better results to be obtained for components with higher acentric factors in later calculations. Details of the method used for determining $F^{(0)}$ are given in the Appendix. The analytical form of $F^{(0)}$ is given by

$$F^{(0)} = 0.39900 + 0.68972/T_r^{2.8} - 0.08872/T_r^{10.5} \qquad (4)$$

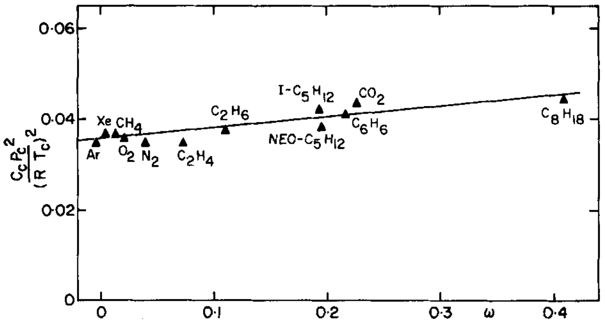

Figure 1. Reduced critical third virial coefficient as a function of acentric factor.

Figure 2 shows the comparison of the experimental data for Krypton with the predictions of De Santis and Grande and of the correlation proposed in this work.

The residual function $F^{(1)}$ required for the representation of the third virial coefficient data of compounds with higher values of the acentric factor was then adjusted. The following expression was found to represent the deviations well.

$$F^{(1)} = \omega(-0.037 + 0.040/T_r^{3.0} - 0.003/T_r^{6.0}) \qquad (5)$$

Combination of Eqs. 2 to 5 gives the final form for the generalized empirical correlation

$$\frac{CP_c^2}{(RT_c)^2} = fC^{(0)}_{(T_r)} + \omega fC^{(1)}_{(T_r)} \qquad (6)$$

with

$$fC^{(0)}_{(T_r)} = 0.01407 + 0.02432/T_r^{2.8} - 0.00313/T_r^{10.5} \qquad (7)$$

and

$$fC^{(1)}_{(T_r)} = -0.02676 + 0.01770/T_r^{2.8} + 0.040/T_r^{3.0} - 0.003/T_r^{6.0} - 0.00228/T_r^{10.5} \qquad (8)$$

NEW GENERALIZED CORRELATION: CLASSICAL CASES

Results for the third virial coefficient obtained with Eq. 6 for nitrogen ($\omega = 0.040$), carbon dioxide ($\omega = 0.225$) and ethane ($\omega = 0.105$), are compared with the predictions of De Santis and Grande and with experimental data in Figures 3 to 5. Table 2 presents a numerical comparison of values of the third virial coefficients for two fluids with large ω values. In all cases, as it was done in Figure 2, for the calculations we have used values of the critical constants and acentric factors as tabulated by Chao, and Greenkorn (1975) for Eq. 6, and the values of the characteristic parameters reported by De Santis and Grande (1979), when using their correlation.

In general there is a good agreement between the simpler correlation presented here, the correlation of De Santis and Grande and the experimental information. For fluids with large acentric factors in the reduced temperature range from 0.8 to 0.9, the correlation of De Santis and Grande produces values that are lower than those obtained with Eq. 6. Reported data in this temperature range are very scarce and it is not possible to reach a valid conclusion with regard to the actual trend. However, as shown in Table 2, the more complex correlation of De Santis and Grande gives a better representation for benzene and octane. For these components, Eq. 6 predicts the maximum of the third virial coefficient to be at a lower reduced temperature. For reduced temperatures higher than 1.6, the two predictive methods diverge in their predictions. The reason for this is that in the generalized correlation

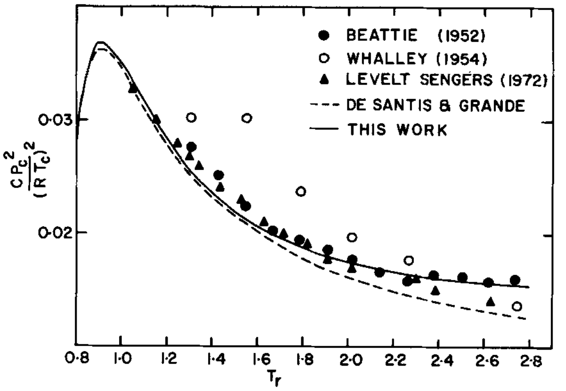

Figure 2. Third virial coefficient of krypton.

developed in this work, the high temperature limit of the third virial coefficient has been allowed to vary with the acentric factor of the component while De Santis and Grande have used a unique limiting value. As it may be observed from Figures 2 to 5, the flexibility of the new correlation usually results in a better agreement with reported experimental data in the high temperature region.

Reported data on the third virial coefficients of components like cyclohexane and neopentane are not well represented by any of the two predictive methods at temperatures below the critical. The average of the absolute percent deviations for the compounds listed on table was 7.23%, excluding cyclohexane and neopentane.

Quantum Gases:

The correlations developed in this work may be applied to quantum gases following the method proposed by Gunn et al. (1966). The same method was used by De Santis and Grande (1979). Gunn et al. (1966) suggested using, for quantum gases, the following temperature dependent effective critical parameters:

$$T_c = \frac{T_c^o}{1 + \dfrac{21.8}{mT}} \qquad (9)$$

$$P_c = \frac{P_c^o}{1 + \dfrac{44.2}{mT}} \qquad (10)$$

where m is the molecular weight and T_c^o and P_c^o are fixed values for each quantum gas. Values of T_c^o and P_c^o for quantum gases used in this work are those reported by Prausnitz (1969). The acentric factor is considered to be zero for all quantum gases.

Table 3 compares experimental third virial coefficients for quantum gases with the predictions obtained using the correlation developed in this work, the correlation of Chueh and Prausnitz (1967a) and the correlation of De Santis and Grande (1979).

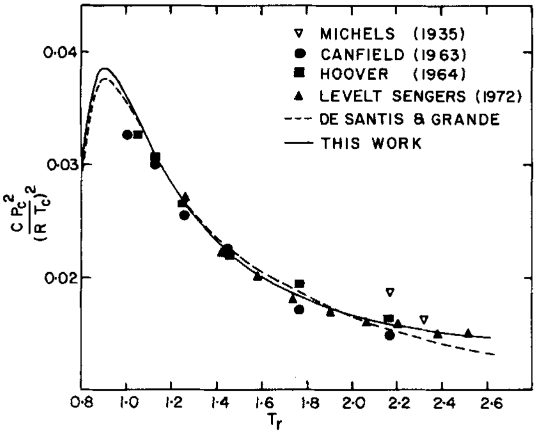

Figure 3. Third virial coefficient of nitrogen.

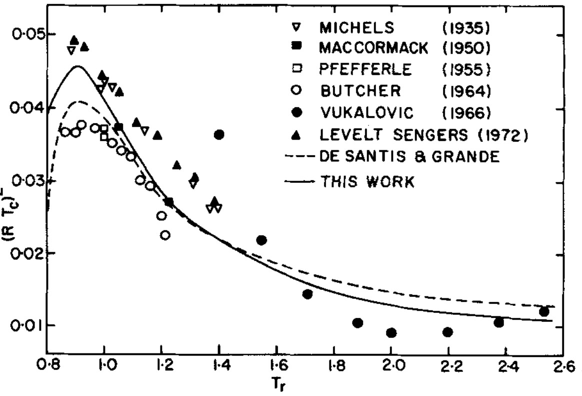

Figure 4. Third virial coefficient of carbon dioxide.

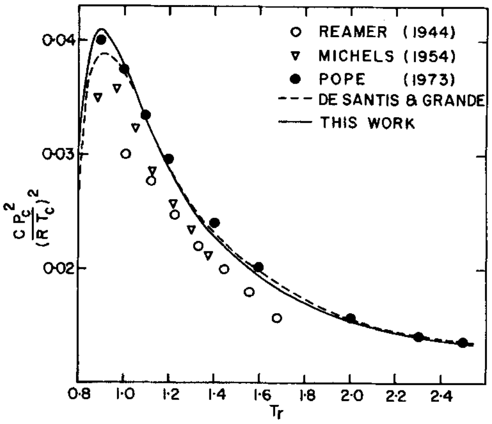

Figure 5. Third virial coefficient of ethane.

For Helium, at temperatures below 10 K, the three methods predict values of the third virial coefficient that are similar among themselves but much higher than the experimental data. At temperatures between 10 and 173.2 K, all three correlations give predictions within the uncertainty of the experimental data. At temperatures above 173.2 K the correlation presented in this work is slightly inferior to the other two.

For Neon, all three correlations give fair estimates of the third virial coefficient in the temperature range from 55.6 to 423.2 K although the correlation of De Santis and Grande (1979) produces values consistently lower than the experimental values.

Finally, for Hydrogen, results obtained with all three correlations are comparable and within the experimental error.

TABLE 2. COMPARISON OF THIRD VIRIAL COEFFICIENT VALUES FOR VARIOUS COMPOUNDS

		Third Virial Coefficient, $(cm^3/mol)^2$			
Compound	t_r	Predicted in This Work	Predicted by De Santis and Grande	Experimental	Source of Experimental Data
Benzene	0.877	41,424	39,111	39,000	Connolly and Kandalic (1960)
	0.912	40,978	41,027	41,000	"
	0.948	39,560	40,527	40,500	"
	0.983	37,744	38,874	39,200	"
	1.019	35,712	36,676	36,800	"
Octane	0.866	194,836	169,862	170,000	Connolly and Kandalic (1960)
	0.902	191,430	180,416	180,000	"
	0.937	183,342	177,623	179,000	"
	0.972	173,087	168,718	170,000	"
	1.010	162,231	157,532	156,000	"

TABLE 3. EXPERIMENTAL AND CALCULATED THIRD VIRIAL COEFFICIENTS FOR QUANTUM GASES

T (K)	Helium C (cm^3/mol)^2				
	Experimental		Calculated		
	Compiled Prausnitz (1969)	Levelt and Sengers (1972)	This work	De Santis and Grande	Chueh and Prausnitz
5	322		1,382	2,314	2,282
6	458		1,169	1,544	1,537
8	513		862	913	913
10	518		683	657	658
12	508		575	522	529
14	498		505	437	454
16	488		457	379	407
20	468		397	308	350
30	417		330	243	287
40	382		302	217	257
60	327	270	277	190	225
80	292	240	266	174	205
173.2	201	160	248	140	165
273.2	156	110	242	123	146
373.2	126	80	240	113	134
573.2	102	—	237	102	120
			Neon		
55.6	900	—	539	531	531
65.3	563	400	447	441	442
90.7	442	400	345	321	342
123.2	309	300	304	257	300
223.2	228	300	279	214	254
273.2	246	300	276	204	241
323.2	234	200	275	195	231
373.2	238	200	273	189	223
423.2	208	—	273	182	216
			Hydrogen		
25	—	1,400	1,722	1,595	1,497
50	—	960	1,034	918	918
100	—	610	602	479	552
150	—	530	527	403	476
200	—	480	499	369	436
300	—	390	477	329	389
400	—	290	467	304	360

EXTENSION TO MIXTURES OF CLASSICAL GASES

The correlation for the third virial coefficient presented in this work may be extended to mixtures using exactly the same method proposed by Chueh and Prausnitz (1967a) and used by De Santis and Grande (1979).

The third virial coefficient of a mixture is given by the following rigorous expression:

$$C = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk} \tag{11}$$

where Chueh and Prausnitz (1967a) have proposed to evaluate C_{ijk} as

$$C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3} \tag{12}$$

and terms of the form C_{ij} are obtained with Eq. 6 using the following values for T_c, P_c and ω:

$$T_{cij} = (T_{ci} T_{cj})^{1/2}(1 - k_{ij}) \tag{13}$$

$$P_{cij} = \frac{4(Z_{ci} + Z_{cj})T_{cij}}{\left[\left(\frac{Z_{ci}T_{ci}}{P_{ci}}\right)^{1/3} + \left(\frac{Z_{cj}T_{cj}}{P_{cj}}\right)^{1/3}\right]^3} \tag{14}$$

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \tag{15}$$

k_{ij}, in Eq. 13 is a binary parameter. Values of k_{ij} used in this work are those reported by Prausnitz (1969).

Experimental information on third virial coefficients of mixtures is scarce and extensive comparisons are not possible. Table 4 presents a comparison between experimental and calculated values for methane-ethylene mixtures in the temperature range from 298.2 to 348.2 K. Results for the correlation of Chueh and Prausnitz (1967a) were not included in Table 4 since the value of the parameter d for ethylene is not available. The predictions obtained with the correlation proposed in this work and with the correlation of De Santis and Grande (1979) are almost identical.

TABLE 4. EXPERIMENTAL AND CALCULATED THIRD VIRIAL COEFFICIENTS FOR MIXTURES OF METHANE AND ETHYLENE

mol % Methane	T = 298.2 K C (cm^3/mol)^2		
	Experimental	Calculated	
	Lee and Edmister (1956)	This Work	De Santis and Grande
0	9,790 ± 2,600	7,342	7,272
0.2	6,540 ± 600	5,998	5,947
0.4	4,100 ± 900	4,852	4,820
0.6	3,250 ± 1,600	3,887	3,872
0.8	2,680 ± 600	3,087	3,086
1.0	2,390 ± 800	2,434	2,447
	T = 323.2 K		
0	7,050 ± 400	6,526	6,412
0.2	5,710 ± 70	5,357	5,282
0.4	4,310 ± 80	4,362	4,315
0.6	3,210 ± 90	3,525	3,499
0.8	2,150 ± 200	2,832	2,817
1.0	1,780 ± 400	2,267	2,258
	T = 343.2 K		
0	5,980 ± 800	5,840	5,706
0.2	4,700 ± 400	4,831	4,744
0.4	3,670 ± 70	3,969	3,912
0.6	2,820 ± 90	3,242	3,201
0.8	1,710 ± 400	2,637	2,601
1.0	1,960 ± 500	2,142	2,101

For the system nitrogen-n-butane at 460.9 K a comparison of the three correlations is possible. Third virial coefficients have been evaluated by Van Ness (1964) from experimental volumetric data measured by Evans and Watson (1956). Table 5 compares the results obtained using the correlations with the experimental values. Within the accuracy of the experimental information, the three correlations produce comparable results.

Mixtures Containing Quantum Gases:

Following Chueh and Prausnitz (1976a), for mixtures containing one or more quantum phases, the effective critical parameters should be used. For the terms of the type C_{ij}, the following mixing rules Chueh and Prausnitz (1967b) proposed to use,

$$T_{cij} = \frac{T^o_{cij}}{1 + \dfrac{21.8}{m_{ij}T}} \tag{16}$$

$$P_{cij} = \frac{P^o_{cij}}{1 + \dfrac{44.2}{m_{ij}T}} \tag{17}$$

TABLE 5. EXPERIMENTAL AND CALCULATED THIRD VIRIAL COEFFICIENTS FOR MIXTURES OF NITROGEN AND N-BUTANE

mol % Nitrogen	T = 460.9 K C (cm^3/mol)^2			
	Compiled	Calculated		
	Van Ness (1964)	This Work	De Santis & Grande	Chueh and Prausnitz
0.0	30,250	30,627	29,262	30,230
0.1	23,953	24,446	23,436	24,325
0.3	14,551	14,793	14,282	15,057
0.5	8,525	8,237	7,993	8,555
0.7	4,819	4,155	4,013	4,421
0.9	2,377	1,924	1,784	2,058
1.0	1,300	1,308	1,153	1,370

Table 6. Experimental and Calculated Third Virial Coefficients for Mixtures of Helium and Nitrogen

$T = 103.15$ K

C (cm^3/mol)^2

mol % Helium	Experimental Hall & Canfield (1970)	Calculated This Work	 De Santis & Grande
1.0	171	259	161
0.8777	262	358	252
0.7529	495	508	391
0.4456	1,286	1,162	1,008
0.3013	1,630	1,647	1,470
0.0	—	3,133	2,891
	$T = 113.15$		
1.0	166	256	157
0.8777	299	358	250
0.7529	379	520	403
0.4456	1,200	1,279	1,144
0.3013	1,765	1,866	1,726
0.0	—	3,711	3,579

where T^o_{cij} and P^o_{cij} are given by Eqs. 13 and 14, respectively, using the characteristic values of Tc^o_i and Pc^o_i and $Zc^o_i = 0.291$, for the quantum gas. The term m_{ij} included in Eqs. 16 and 17 is given by

$$\frac{1}{m_{ij}} = \frac{1}{2}\left(\frac{1}{m_i} + \frac{1}{m_j}\right) \tag{18}$$

ω_{ij} is given by Eq. 15 considering $\omega = 0$ for quantum gas.

For the calculations with the correlation of De Santis and Grande (1979), the mixing rules used by the authors have been retained.

Table 6 compares the predictions with experimental values for the system helium-nitrogen at two temperatures. In the helium rich section the equation of De Santis and Grande appears to give better predictions. However, a comparison of the values of the third virial coefficients of pure helium given in Table 3 with those of Hall and Canfield (1970), Table 6, shows that the latter are on the lower side and favor the comparison with the calculated values given by the correlation of De Santis and Grande. This comparison also shows the large possible error in experimental values of the third virial coefficients.

AUGMENTED VIRIAL EQUATION OF STATE

Although it is not the purpose of this paper to discuss particular applications of the augmented virial equation of state, a brief comment on its behavior and potentialities is in order.

The pressure explicit virial equation of state, truncated after the third virial coefficient, Eq. 1, can now be used for nonpolar components in a generalized form. For the second virial coefficient we adopt the generalized correlations of Pitzer and Curl (1957) or of Tsonopoulos (1974, 1979). They have the general form

$$\frac{BP_c}{RT_c} = fB^{(0)}_{(T_r)} + \omega\, fB^{(1)}_{(T_r)} \tag{19}$$

Equation 6 for the third virial coefficient has the same functional form.

Clearly, the P-v-T behavior of a fluid in the range of applicability of Eq. 1, $v > (4/3)v_c$, can be described with these characteristic parameters: the critical temperature, the critical pressure and the acentric factor. However, if the equation is written in reduced form, four characteristic parameters are required to describe the "corresponding states" of nonpolar fluids, i.e., T_c-P_c, Z_c and ω. This interesting fact was previously observed by Bienkowski et al. (1973), who also observed that only for normal fluids Z_c and ω are not independent. Notably, this will not be the case if the critical volume were used as parameter for both the second and the third virial coefficients.

In a study of van der Waals' type of equations of state, Martin (1967) found that replacement of critical volume by critical pressure as characteristic parameters produced an improvement in the performance of the equations. These findings of Bienkowski et al. (1973) and of Martin (1967) support the argument of the present authors to use T_c, P_c and ω as characteristic parameters.

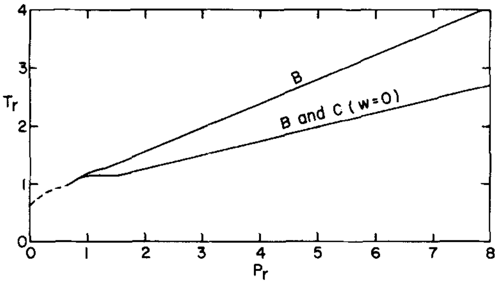

Figure 6. Applicability range of the virial equation of state truncated after the second and after the third virial coefficients.

The enhanced applicability range of the augmented virial equation is presented in Figure 6. The lines were drawn considering the acentric factor to be zero. Surprisingly, a positive acentric factor seems to allow a larger range of applicability of the equation. Figure 6 represents, then, a conservative estimate for most fluids.

For some practical uses, the volume explicit virial equation of state has been preferred. From the pressure explicit form, truncated after the third virial coefficient, as a first approximation we obtain

$$V = \frac{RT}{P}\left(1 + \frac{B}{RT}P + \frac{C - B^2}{(RT)^2}P^2 + \frac{2B^3 - 3BC}{(RT)^3}P^3 + \ldots\right) \tag{20}$$

Preliminary calculations have shown that for reduced temperatures above 2, Eqs. 1 and 10 perform comparably in the augmented range of applicability shown in Figure 6. For reduced temperatures below 2, Eq. 1 is recommended.

ACKNOWLEDGMENTS

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APPENDIX: DEVELOPMENT OF A CORRELATION FOR $F^{(0)}$

According to Eq. 3 of the text, for krypton ($\omega = 0$)

$$(C/C_c) = F^{(0)}_{(T_r)} \tag{A.1}$$

where the function $F^{(0)}_{(T_r)}$ should meet the following minimum conditions in order to give a satisfactory prediction of the third virial coefficient of krypton.

1) The value of $F^{(0)}_{(T_r)}$ must be unity at $T_r = 1$.

2) The value of $F^{(0)}_{(T_r)}$ should be a maximum in the vicinity of $T_r = 0.9$. The value of T_r that produces the maximum in $F^{(0)}_{(T_r)}$ is designated by T_r'.

3) At a reduced temperature in the vicinity of $T_r = 0.74$, the value of $F^{(0)}_{(T_r)}$ should be zero. The value of T_r for which $F^{(0)}_{(T_r)} = 0$ is called T_r''.

4) At $T_r \to \infty$, $F^{(0)}_{(T_r)}$ should tend to a constant positive value of about 0.4. This constant positive value is designated by A_0.

Probably the simplest function capable of meeting all of the above conditions is

$$F^{(0)}_{(T_r)} = A_0 + \frac{A_1}{(T_r)^{n_1}} + \frac{A_2}{(T_r)^{n_2}} \tag{A.2}$$

From conditions 1 to 3, we obtain

$$A_0 + A_1 + A_2 = 1 \tag{A.3}$$

$$\frac{n_1 A_1}{(T_r')^{n_1+1}} + \frac{n_2 A_2}{(T_r')^{n_2+1}} = 0 \qquad \text{(A.4)}$$

and

$$A_0 + \frac{A_1}{(T_r'')^{n_1}} + \frac{A_2}{(T_r'')^{n_2}} = 0 \qquad \text{(A.5)}$$

Condition 4 is directly given by Eq. A.2.

$$A_0 \approx 0.4 \qquad \text{(A.6)}$$

Equations A.2 to A.5 may be rearranged to give

$$A_1 = \frac{(T_r'')^{n_1+n_2}}{(T_r'')^{n_2} - (T_r'')^{n_1}} \left[\frac{1 - A_0}{(T_r'')^{n_1}} + A_0\right] \qquad \text{(A.7)}$$

$$\frac{(1 - A_0 - A_1)}{T_r{}^{n_1}} + \frac{A_1}{(T_r)^{n_1}} - F^{(0)}_{(T_r)} + A_0 = 0 \qquad \text{(A.8)}$$

$$\frac{n_1(1 - A_0 - A_1)}{(T_r')^{n_1+1}} + \frac{n^2 A_1}{(T_r')^{n_2+1}} = 0 \qquad \text{(A.9)}$$

The values of A_0, T_r' and T_r'' were fixed at values close to those specified by the conditions 1 to 3. By choosing one experimental point, for example, T_r, $F^{(0)}_{(T_r)}$ was evaluated from Eq. A.1. A set of $\{n_1,n_2\}$ values satisfying Eqs. A.7 and A.8 and a set of $\{n_1,n_2\}$ values satisfying Eqs. A.7 and A.9 were obtained. The intercept of the curves generated by plotting n_1 vs. n_2 for each set, gives the pair of values (n_1,n_2) satisfying simultaneously Eqs. A.7, A.8 and A.9. These values are somewhat dependent on the values of A_0, T_r' and T_r'' and on the choice of the experimental point. Different combinations were studied and the results of each were tested against experimental information using Eqs. A.1 and A.2. The numerical values reported in Eq. 4 of the text are those that gave the best overall fit of the experimental data.

NOTATION

A_0,A_1,A_2 = adjustable parameters, Eq. A.2
B = second virial coefficient
C = third virial coefficient
d = additional parameter, characteristic of compound, used by Chueh and Prausnitz (1967a)
$F^{(0)}$ = generalized function of reduced temperature, Eq. 4
$F^{(1)}$ = generalized function of reduced temperature and of acentric factor, Eq. 5
$\int_C^{(0)}, \int_C^{(1)}$ = generalized functions of reduced temperature used in the correlation of the reduced third virial coefficient, Eqs. 6 to 8
$\int_B^{(0)}, \int_B^{(1)}$ = generalized functions of reduced temperature used in the correlation of the reduced second virial coefficient
m = molecular weight
n_1,n_2 = adjustable exponents, Eq. A.2
P = absolute pressure
k = binary interaction constant
R = gas constant
T = absolute temperature
v = molar volume
y = mole fraction
z = compressibility factor
ω = acentric factor

Subscripts

c = critical conditions
r = reduced conditions
i,j,k = components

Superscript

o = characteristic parameters for quantum gases

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Corrected Flowrates Estimation by Using θ Convergence Promoter for Distillation Columns

The main task of the θ convergence promoter is to afford a better estimate of liquid and vapor molar fractions in each tray of the column.

The assumptions implied by the promoter prove to be reliable for conventional columns, while they may cause numerical instability when dealing with nonconventional configurations. In these cases, corrected molar fractions may be computed only after making a supplementary assumption, which in principle is not unique. So, the paper presents a new methodology which gives rather satisfactory results.

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SCOPE

The θ method for the simulation of distillation column is defined as a combination of numerical algorithms with a convergence promoter.

The former contribute to the iterative solution of the system of equations describing the column model. The latter (so far called as "θ-convergence promoter") accelerates the convergence of the whole numerical procedure by adopting the well-known θ multipliers. These can be distinguished into a primary θ multiplier and additional θ multipliers. Both of them refer to

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