Virial Coefficients for Argon, Methane, Nitrogen, and Xenon

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The second, third, and fourth virial coefficients for argon, methane, nitrogen, and xenon have been established by various methods to satisfy experimental compressibility data and also to satisfy graphical computations of the property deviation relationships of Δu^o and Δh^o.

Although values of the second virial coefficient found in the literature are fairly accurate, there is always some difference in the values from one investigator to another. The differences become even more noticeable when the higher virials C and D are considered, emphasizing that the basic data are not exactly correct and therefore the method of analysis is a strong factor. In this paper several methods of analysis were used first to establish and then to check the values reported herein. A smoothing technique based upon corresponding states entered as a judgment factor.

The calculated coefficients exhibit a range of values that will satisfy compressibility data within experimental error over a specified density interval; therefore the first step was to establish these maxima and minima ranges. The second step was to calculate temperature derivatives of the coefficients from graphically established property deviations such as internal energy or enthalpy. These temperature derivatives were graphically integrated and the resulting B, C, or D function overlaid on the compressibility range values. Since exact alignment was rare, adjustments were made by recalculating the coefficients by other methods and by an error analysis based upon a generalizing technique (described subsequently). Finally B, C, D values were selected that satisfied all of the basic data within experimental error.

A major difficulty of most calculational methods is that the values of the higher virials are dependent upon the values assigned to the lower virials. Thus B (and dB/dT) must be rather exactly established before proceeding to C (and dC/dT), since any error in B magnifies greatly the errors in C and D. For this reason the B and dB/dT values for each gas were generalized* by the de Boer principle of corresponding states as a test of the basic data and as a judgment factor in selecting the true B values. The third virial coefficients for each gas were then calculated but based on specific values of B (and dB/dT) derived from the generalized B (and dB/dT) curve. Similarly the fourth virial coefficient was based on the generalized B and calculated C (with the exception of a few isotherms, where because of the scatter in C the generalized C value was selected).

Note that the foregoing procedure is merely a smoothing or averaging technique since the final values of the virial coefficients will yield the original pvT, Δu^o, and Δh^o data within the experimental error.

The methods to be discussed apply to any function, $f(\rho)$. Compressibility data are represented as

$$f(\rho) \equiv z - 1 = B\rho + C\rho^2 + D\rho^3 + \ldots \tag{1}$$

while for internal energy deviation

$$f(\rho) \equiv \Delta u^o = -RT^2 \left[\frac{dB}{dT}\rho + 1/2\frac{dC}{dT}\rho^2 + \ldots \right] \tag{2}$$

Hence in general

$$f(\rho) = A_1\rho + A_2\rho^2 + \ldots \tag{3}$$

is defined such that B or dB/dT can be found from the value A_1, C or dC/dT from A_2, etc.

METHODS OF DATA ANALYSIS

Linear Approximation

A linear approximation method is outlined by Bird (*4*) and was used by McClure (*5*) for hydrocarbons and by Liley (*6*) for steam. The procedure requires plotting the quantity $(z - 1)/\rho$ vs. ρ at constant T. It then follows since

$$\lim_{\rho \to 0} \frac{z - 1}{\rho} = B \tag{4}$$

that the intercept with the ordinate yields the second virial coefficient B. In the low-density region the data approximate a straight line so that

$$\frac{z - 1}{\rho} \doteq B + C\rho \tag{5}$$

yielding an intercept B and a slope C. As a second approximation

$$\frac{z - 1 - B\rho}{\rho^2} \doteq C + D\rho \tag{6}$$

Unfortunately slopes such as C and D in Equations (5) and (6) may not agree with the intercept values calculated, say, by the limit of Equation (6). The disagreement results from the influence of the neglected terms and from error in the previous coefficient. The greatest restriction to methods of this type is the accuracy of the data, especially in the low-density region. Michels' values of nitrogen, argon, methane, and xenon were sufficiently precise in most instances, although for temperatures below 0°C. his low-density data for nitrogen do not approximate a straight line. This same scatter was more pronounced in the data of Din (*19*, *20*) and of Sage and Lacey (*21*) and occurred also at higher temperatures, making it necessary to extrapolate the linear relationship from a region of higher density. Considerably more scatter is shown by the second approximation, Equation (6).

Where the data seemed consistent, Equation (5) was the primary means for calculating the B and dB/dT values in this paper. This method was also used to check the high-temperature C values of argon and nitrogen.

Least-Square Approximation Method

The limitations in the available data usually do not justify an elaborate procedure. Assume that the values of

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* Method is described in reference *1*.

A_1 are established, say by the linear approximation method. A least-square criterion

$$I = \Sigma[f(\rho) - A_1\rho - A_2\rho^2]^2$$

can then be applied to the tabulated data for any isotherm. Values of A_2 and the mean-square deviation are calculated successively for one additional property value $[\rho, f(\rho)]$ beginning at the smallest tabulated value of ρ. A region of approximately constant A_2 and constant deviation values will be noted, and this region defines the best value for A_2. The tabulated property can be transferred to computer data processing cards and all of the calculations accomplished with a minimum of plotting or manual calculation.

This method yielded satisfactory results (in general somewhat higher values than the linear approximation method) and has the distinct advantage of simplicity. Although other methods were also used when doubt existed, the C, dC/dT, D, and dD/dT functions in this paper are based primarily on the least-square method.

Least-Square Power Series Method

Many of the reported values for the virial coefficients in the literature were obtained by a least-square fit of a truncated power series in density or pressure to experimental pvT measurements. Probably the best-known values are those of Holborn and Otto (*22, 23, 25, 26*), Kamerlingh Onnes (*22, 23, 24*), Keesom (*22, 23*), and Michels (*7* to *16*). It is generally concluded that the coefficient of p or ρ is within 1 to 4% of the correct value of B. The higher virials however are not found to such a high degree of accuracy. Michels (*18*) has shown the effect of increasing the degree of the fitting polynomial for the same density range on the values of the coefficients; for example C may change as much as 100% with a change in B of only 4%.

Orthogonal Polynomial Method

The interdependence of the coefficients can be avoided by the method of orthogonal polynomials, as illustrated by the results of Opfell, Pings, and Sage (*27*) for propane. A similar method was tested on the compressibility data for nitrogen with pressure as the independent variable and yielded excellent values for B and disappointing values for C and D. It seems that even though the derived series function may closely approximate the experimental data, the coefficients of the series may or may not converge to the correct values of B, C, D, etc. One reason for the failure is that the method demands data at specified intervals and thus requires cross plotting of the available data. Since the data have some scatter, the cross plotting leads to error. Also error enters the calculation procedure as a result of computer round off of intermediate results. In general the calculation errors did not noticeably affect the solution until the sixth or seventh term of the orthogonal series.

Zero-pressure Joule-Thomson Coefficient Method

The Joule-Thomson coefficient is defined as

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_h$$

With the virial equation of state and at zero pressure it can be shown that

$$\frac{dB}{dT} - \frac{1}{T}B = \frac{\mu^o c_p{}^o}{T} \qquad (7)$$

When B_x is known at a temperature T_x

$$B = T\left[\frac{B_x}{T_x} + \int_{T_x}^{T} \frac{\mu^o c_p{}^o}{T^2}\,dT\right] \qquad (8)$$

In checking the calculated B and dB/dT values for nitrogen (from compressibility and internal energy data) against the zero-pressure J-T coefficients calculated by Michels (*17*), and the experimental values of Ishkin and Kagener (*29*), close agreement was found down to a temperature of approximately 0°C. Below this temperature the calculated B values gave slightly higher values of the J-T coefficient. Because of this discrepancy Equations (7) and (8) were the means to calculate B and dB/dT values below 0°C. The resulting values agree closely with those of Holborn and Otto, Kamerlingh Onnes, and van Itterbeck, and also when generalized, agreed with the values for argon derived from Δu^o data (*30*).

PROPERTY DATA

The selection of the best sources of experimental data is vital in establishing the virial coefficients. Since data for nitrogen were most plentiful, a comparison study of various sources was made by Panton (*31*):

Nitrogen

Source	Property	Temp.	Press. or density
Michels (*14* to *16*)	z, Δu^o, Δh^o, Δs^o, Δg^o	−125° to 150°C.	0 to 760 Amagat
Din (*19*)	z, h, c_p, s	90° to 700°K.	1 to 10,000 atm.
Sage (*21*)	z, h, f, s,	0° to 800°F.	0 to 15,000 lb./sq.in.abs.
Roebuck (*32* to *33*)	μ	300° to 180°C.	1 to 200 atm.
Bloomer (*34*)	z (chart)	500° to 300°F.	0 to 1,500 lb./sq.in.abs.

Michels calculated the internal energy and enthalpy deviations by graphical analysis of compressibility data. His data (150° to 0°C.) were extended to −125°C. by inclusion of the data of Benedict (*35, 36*) and the B values of Holborn-Otto (*25*) and Kamerlingh Onnes (*24*). As a matter of interest it is in this extension of the range (below 0°C.) where the greatest errors were observed. Michels estimated an error in pv of ½% in this region but only 1/100% above 0°C. For his property values he estimated 0.02 to 0.2% error above 0°C., increasing to 2% for the lower temperatures. With the exception of the low-temperature values greatest weight was given to Michels' data in calculating the virial coefficients.

To compare and to extend the coefficients calculated from Michels' data a number of sources were considered: Keesom (*37*), Burnett (*38*), Sage-Lacey (*21*), and Din (*19*). Panton concluded that the data of Sage-Lacey and Din were best suited for this purpose. The Din compilation is based on the data of Michels, Holborn-Otto, Kamerlingh Onnes, van Urk, and Benedict and includes regions where there was a significant lack of basic data. These regions were bridged by Din in a manner he describes as "judicious guesswork." The agreement of B with other sources (even in the region of guesswork) is excellent. Values of C and D calculated from the Din compilation also show very good agreement with those calculated from other sources.

ARGON

Argon was selected as the primary monatomic gas to be studied because of the amount of data available. Greatest weight was given to Michels' data, although the compilations of Din were used as checks (based upon data of Holborn-Otto, Holborn-Scultze, Otto, Tanner-Masson, Michels, and Roebuck).

Argon

Source	Property	Temp.	Press. or density
Michels (*7* to *10*)	z, Δu^o, Δh^o, Δs^o	−140° to 150°C.	0 to 640 Amagat
Din (*20*)	z, h, s, c_p	90° to 600°K.	1 to 5,000 atm.
Roebuck (*39*)	μ	−150° to 300°C.	1 to 200 atm.
Whalley (*40*)	z, c_p, c_v Δh^o, Δs^o, μ	−100° to 600°C.	0 to 80 atm.

The results of Whalley are included to illustrate a different approach to the evaluation of virial coefficients. Whalley and Schneider (*41*) found the virial coefficients B and C by means of the Burnett expansion method. Their values for B are in close agreement with those reported herein, but their C values are higher. Since D values are positive in the temperature range considered by Whalley, his C values can be interpreted as including the effect of D. The property values calculated from the Whalley values are most probably in error for temperatures less than 350°K. This is indicated by his function for dC/dT which gives values from two to three times greater than those derived from Michels' Δu^o data. Thus from Equation (2) his calculated Δu^o will be too small where the second term becomes appreciable.

METHANE

Nelson (*2*, *42*) found that the generalized compressibility values of methane agreed well with those of nitrogen. Consequently methane was selected as another gas which would aid in developing a generalized equation of state (*1*):

Methane

		Range	
Source	Property	Temp.	Density
Michels (*12*, *13*)	z, Δg^o, Δh^o, Δu^o, Δs^o	0° to 150°C.	0 to 225 Amagat
Tester (*19*)	z, s, h, c_p f/p, μ	130° to 470°K.	1 to 1,000 atm.
Sage (*21*)	z, f, h, s	70° to 460°F.	0 to 10,000 atm.

As before greatest weight was given to the work of Michels. Tester's compilation is based on the works of Michels, Kvalnes-Gaddy, Keyes-Burks, and Olds-Reamer-Sage-Lacey. Since Tester's data below −70°C. cannot be considered precise, virial coefficients were calculated only for higher temperatures. Generalized values were then used to extrapolate into the low-temperature region. The results of this procedure should be more precise than the results of Tester in this region.

XENON

Michels (*11*) recently (1956) published the thermodynamic properties of xenon, calculated from pvT measurements.

Xenon

		Range	
Source	Property	Temp.	Density
Michels (*11*)	z, Δu^o, Δh^o, Δs^o	0° to 150°C.	0 to 520 Amagat

The exact generalization (*1*) of xenon and argon indicated the excellent precision of Michels' data.

RESULTS

The virial coefficients found in this work are summarized in Table 1. These values were taken from graphs of the calculated virial coefficients. The maximum deviation in the second virial coefficient was within 1 to 2 cc./g.-mole. As a result of the procedure of generalizing the B plots the maximum scatter in the C and D plots was reduced to 5 or 6%. In general the scatter in the calculated C values (2 to 3%) was somewhat less than that for D (2 to 5%). With the exception of the nitrogen D below 0°C. the generalized D plot fell within the range of the calculated coefficients. This exception is shown in Table 1. The principle reason for this difference is the lesser precision of the low-temperature data, although some effect of the lower coefficients (B, C) is probably included. (Consequently the low-temperature nitrogen coefficients were not used to establish the generalized curves in reference *1*.) The temperature derivatives are not included in this paper since they can be readily obtained from the tables of reference *1*.

The calculated second and third virial coefficients were compared with values of other investigators. The second virial coefficient was generally in close agreement (within 2 cc./g.-mole) except for Schneider's xenon values (*43*) below 350°K. For example at 0°C. a difference of 7 cc./g.-mole was noted. However in this region the calculated B values agreed precisely with those given by Beattie (*44*). The comparison of the nitrogen C values indicated the same trend as Holborn-Otto and Onnes, although the Holborn-Otto values were generally somewhat higher and those given by Onnes were lower. On the other hand the nitrogen C values of the Bureau of Standards (*45*) suggests a completely different curve even though the B values were in close agreement. Favorable agreement in magnitude and shape was found between the calculated xenon third virial coefficients and those of Beattie. As in the case of B, Schneider's values at the lower temperatures deviated considerably from the calculated results. Since Whalley and Schneider included the Holborn-Otto argon C values in their temperature function, a close agreement exists between these sources. Nevertheless from the disagreement between their results and those of this work (and of Michels and of Onnes) it appears that their results are too large (probably including the effect of D).

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TABLE 1. VIRIAL COEFFICIENTS

NITROGEN

Temperature, °K.	B, cc./g.-mole	$C \times 10^{-3}$ (cc./g.-mole)^2	$D \times 10^{-3}$ (cc./g.-mole)^3	
600	21	1.13	34.1	
500	17	1.17	38.8	
400	9	1.22	41.3	
350	3	1.27	40.2	
300	−5	1.38	36.5	
260	−14	1.53	29.1	30.8*
220	−28	1.74	15.5	19.6*
180	−49	2.15	−5.8	8.1*
140	−84	2.97	—	−6.3*
120	−113	3.54	—	
100	−160	—	—	
80	−231	—	—	

* From generalized D curve.

ARGON

Temperature, °K.	B, cc./g.-mole	$C \times 10^{-3}$ (cc./g.-mole)^2	$D \times 10^{-3}$ (cc./g.-mole)^3
600	13	0.74	22.4
500	7	0.760	23.4
400	−1	0.830	22.2
350	−7	0.900	20.0
300	−15	1.02	16.7
260	−25	1.16	12.8
220	−39	1.39	7.90
180	−60	1.79	1.70
160	−76	2.11	−1.90
140	−99	2.38	—
120	−131	—	—

METHANE

Temperature, °K.	B, cc./g.-mole	$C \times 10^{-3}$ (cc./g.-mole)^2	$D \times 10^{-3}$ (cc./g.-mole)^3
500	−2	1.55	49.0
450	−8	1.66	44.3
400	−16	1.81	38.4
350	−27	2.01	30.1
300	−43	2.36	18.9
250	−65	2.92	4.90
200	−104	3.97	−12.7

XENON

Temperature, °K.	B, cc./g.-mole	$C \times 10^{-3}$ (cc./g.-mole)^2	$D \times 10^{-3}$ (cc./g.-mole)^3
450	−52	3.33	38.5
400	−70	3.83	24.3
350	−94	4.53	7.6
300	−128	5.59	−11.3
270	−156	—	—

NOTATION

A = function, in general
B, C, D = virial coefficients (temperature functions)
c_p = specific heat
f = fugacity
g = Gibbs free energy
h = enthalpy ($\Delta h^o = h - h_{\text{ideal}}$)
R = universal gas constant
s = entropy ($\Delta s^o = s - s_{\text{ideal}}$)
T = absolute temperature
u = internal energy ($\Delta u^o = u - u_{\text{ideal}}$)
z = compressibility factor ($z = pv/RT$)
ρ = density
μ = Joule-Thomson coefficient

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A Generalized Virial Equation of State Derived from Experimental Data

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Generalized virial coefficients B^*, C^*, D^*, and their derivatives have been established to satisfy experimental compressibility and Δu^0, Δh^0 data for spherically-symmetrical, nonpolar gases.

The generalized virial equation of Bird-Spotz (*1*)

$$z = \frac{p^*}{\rho^* T^*} = 1 + B^*\rho^* + C^*\rho^{*2} \qquad (1)$$

$$B^* = \frac{B}{b_0} \qquad C^* = \frac{C}{b_0^2}$$

$$p^* \equiv \frac{p}{(R/b_0)(\epsilon/k)} \qquad \rho^* \equiv b_0\rho \qquad T^* \equiv \frac{T}{\epsilon/k} \qquad (2)$$

is remarkably accurate at low densities where two virial coefficients B^* and C^* are sufficient. Since the equation rests upon the theoretical potential function of Lennard-Jones, it cannot be expected that the same degree of accuracy will be obtained by merely adding on additional virials, obtained from theoretical calculations such as those of Barker and Monaghan (*2*) or of Boys and Shavitt (*3*). However the compressibility charts of Nelson and Obert (*4, 5*), based on the same (de Boer) principle of corresponding states which underlies the Bird-Spotz equation, showed that a satisfactory correlation of experimental compressibility data could be obtained over a wide density range, a range dictated by many virial coefficients. These charts suggest that assigning constant values to the reduction parameters ϵ/k and b_0 is an adequate means for at least the D^* and E^* coefficients.

Numerous values of the virial coefficients derived from experimental compressibility data can be found in the literature. All such data in general are open to question for the following reasons: the errors in the higher virials C, D, etc. are magnified by any error in the values assigned to B, C, etc.; and although it is the temperature-derivative values of the coefficients that dictate the isothermal changes in Δu and Δh, the coefficients were derived almost entirely from compressibility measurements. Because of these faults it was necessary to calculate by various methods the virial coefficients B, C, and D, and their temperature derivatives for argon, methane, nitrogen, and xenon (*6*). From previous work (*7*) it is believed that these gases could well form the nucleus for an experimental generalized virial equation. The method briefly was first to establish maxima and minima ranges of the coefficients that would fulfill compressibility demands. The second and more important step was to calculate the temperature derivatives of the coefficients from graphically established property deviations such as those for internal energy and enthalpy. These derivative curves were then graphically integrated, and the resulting B, C, or D functions were fitted to the compressibility range requirements. With this procedure the ability of the virial coefficients to measure both compressibility and other property data was enhanced.

THE GENERALIZED TABLES

To establish a generalized equation of state from experimental virial coefficients for a particular gas requires an arbitrary assignment of values to the so-called *force constants* ϵ/k and b_0. The assignment was made so that the final generalized virial coefficients could be easily compared with the theoretical values of Bird-Spotz (*1*) to illustrate the areas of agreement with the Lennard-Jones potential.

Argon was chosen to be the base gas because a monatomic gas should fit best the de Boer principle of corresponding states, and reliable property data were available over a fairly wide temperature range (—140° to 150°C.). The Boyle temperature is never precisely defined by the B virial (404° to 412°K. for argon) because of the flatness of the curve and the scatter of experimental data. Hence a graphical method was devised for deriving the Boyle temperature directly from compressibility values. Values of density vs. temperature for $z = 1$ were plotted from the compressibility data of Michels (*8 to 11*) and Din (*12*). The plot is linear and when extrapolated to zero

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