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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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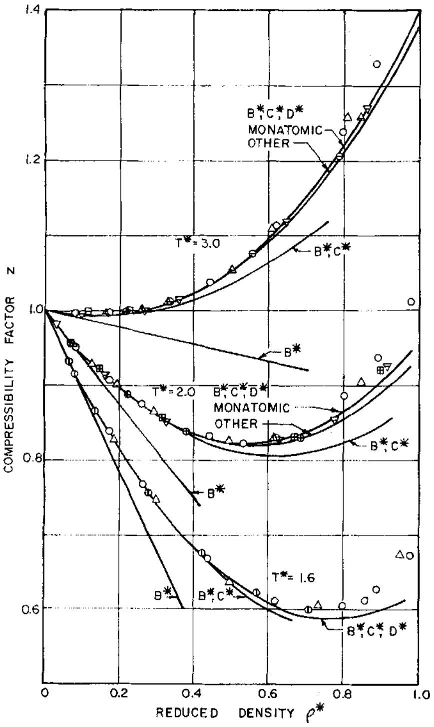

Fig. 1. Compressibility data comparison with values calculated from the generalized tables. (Michels: ○, argon; circle with line across, nitrogen; circle with cross, methane), (Din: △, argon; triangle with line across, nitrogen), (Bloomer: box with line across, nitrogen), (Tester: box with cross, methane), Sage-Lacey: triangle pointing down with line across, nitrogen; triangle pointing down with cross, methane).

density gives a Boyle temperature of 408°K. Bird (*13*) shows the Lennard-Jones generalized Boyle temperature to be 3.417. It follows from the definition of T^*

$$\left.\frac{\epsilon}{k}\right]_{\text{argon}} = \left.\frac{T_{\text{argon}}}{T^*}\right]_{\text{Boyle}} = \frac{408}{3.417} = 119.4\text{°K.} \qquad (3)$$

The volume parameter b_0 was assigned from the value of dB/dT for argon at 408°K. and Bird's value of dB^*/dT^* at $T^* = 3.417$:

$$b_0 \equiv \frac{B}{B^*} = \frac{\epsilon}{k}\,\frac{dB/dT}{dB^*/dT^*} =$$

$$119.4\,\frac{0.100}{0.2373} = 50.3 \text{ cc./g.-mole} \qquad (4)$$

The selection of the force constants for nitrogen, methane, and xenon is discussed in the following section.

Argon and nitrogen serve as the primary gases for Table 4: argon (ϵ/k = 119.4°K., b_0 = 50.3 cc./g.-mole) in the range T^* = 1.11 to 3.54 and nitrogen (ϵ/k = 96.3°K., b_0 = 63.6 cc./g.-mole) for the range T^* = 2.83 to 6.0. In addition methane (ϵ/k = 149.8°K., b_0 = 68.7 cc./g.-mole) data were used from T^* = 1.83 to 2.82 and xenon (ϵ/k = 230.5°K., b_0 = 80.0 cc./g.-mole) for the range T^* = 1.18 to 1.84.

The precise generalization of the monatomic gases was evident from the calculated coefficients, while nitrogen and methane required a slightly lower D^* curve to fit better the experimental compressibility data. The correlation of the experimental compressibility data (Figure 1 as an example) is excellent to a reduced density ρ^* of 0.4 to 0.5 (at low reduced temperatures), but at higher densities the nitrogen and methane values, although correlating each other, fall below the monatomic gas curve. This deviation at higher densities explains the larger values of D^* for the monatomic gases. Also because of the good correlation at lower densities single functions are found for B^* and C^* for all gases. Fortunately the derivatives of the virial coefficients showed a close correlation which indicated that the virial coefficient temperature functions of nitrogen and methane must be similar to those for the monatomic gases. Hence only one function is necessary for each of the virial coefficient derivatives, and the equation of state for the monatomic gases will differ from that for the other gases by only an additional constant in the D^* term.

SELECTION OF FORCE CONSTANTS

Reference *13* discusses methods for estimating the force constants and lists values for the Lennard-Jones model. The values adopted for this paper are shown in Table 1.

Although most of the values of ϵ/k and b_0 in Table 1 are average or adjusted values, they can be predicted quite closely by several methods. A means was devised for finding the Boyle temperature of a gas based on the minima exhibited by the isotherms on a compressibility chart. Graphs of minimum z vs. temperature were constructed for argon, xenon, nitrogen, and methane. The Boyle temperatures could not be read from these charts, since the curves become asymptotic to $z = 1$ as the Boyle temperature was approached. However for each value of z minimum the temperature difference Δ between argon and a second gas can be found and plotted against the argon temperature. These plots were found to be linear, and when extrapolated to 408°K. (Boyle temperature of argon) the difference between the Boyle temperature of the gas and that of argon can be read. The Boyle temperatures obtained by this method are also tabulated in Table 1. Too, by extrapolating the plots to 150.72°K. (critical temperature of argon) the critical temperatures of Table 1 were checked (except that for xenon which had an extrapolated value of 290.8°K.). Because of the linearity it follows that

$$T_{\text{gas}} = T_{\text{argon}} + \Delta]_{\text{minima of } z} \qquad (5)$$

while by definition at the same T^* (or same minimum z)

$$\left.\frac{T_{\text{gas}}}{T_{\text{argon}}}\right]_{\text{minima of } z} = \frac{\epsilon/k]_{\text{gas}}}{\epsilon/k]_{\text{argon}}} \qquad (6)$$

Thus Equations (5) and (6) may be combined in the form,

$$\epsilon/k]_{\text{gas}} = \epsilon/k]_{\text{argon}}\left(1 + \frac{\Delta}{T_{\text{argon}}}\right) \qquad (7)$$

Since Δ as a function of T_{argon} can be derived from the Δ plots, Equation (7) allows ϵ/k for any gas to be formu-

TABLE 1. FORCE CONSTANTS AND BOYLE TEMPERATURES

	ϵ/k, °K.	b_0, cc./ g.-mole	T_B, °K.	Suggested temperature range
Air	101.0	60.1		>0°C.
	104.0	58.7		<0°C.
Argon	119.4	50.3	408	all
Carbon monoxide	101.4	65.1		>0°C.
	104.4	63.5		<0°C.
Krypton	166.8	62.2	570	all
Methane	149.8	68.7	509	−60° to 240°C.
Neon	35.2	26.5	120.2	all
Nitrogen	96.3	63.6	329	>0°C.
	99.1	62.1		<0°C.
Oxygen	118.1	52.2		>0°C.
	121.6	50.9		<0°C.
Xenon	230.5	80.0	787.4	all

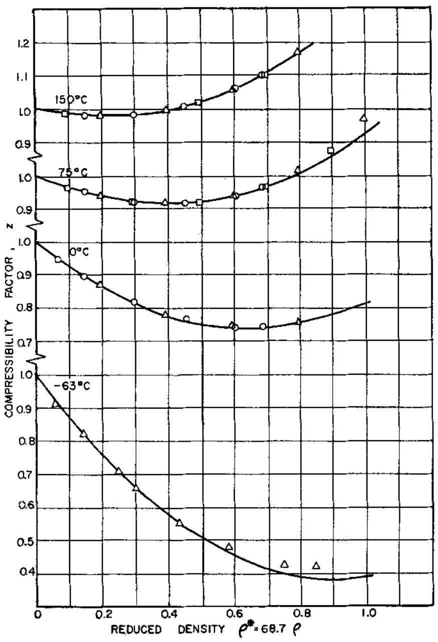

Fig. 2. Methane compressibility data compared with values calculated from the generalized tables. (Michels: ○), (Tester: △), (Sage-Lacey: □), (B*, C*, D* : ——).

lated as a temperature function. It was found that ϵ/k for xenon was constant, which indicated that the monatomic gases were precisely generalized by the de Boer principle of corresponding states in the regions considered.

With a value assigned to ϵ/k the force constant b_0 can be derived by the method suggested in Equation (4) from the calculated values of B and/or dB/dT. However this requires knowledge of the second virial coefficient and the generalized second virial coefficients for a number of temperatures so that an average value can be assigned. Essentially the same result is obtained, more conveniently, by invoking the modified law of corresponding states

$$\rho_{c'}b_0]_{\text{gas}} = \rho_{c'}b_0]_{\text{reference gas}}$$

so that

$$b_0 = \frac{\rho_{c'}b_0]_{\text{reference gas}}}{\rho_{c'}} \tag{8}$$

and

$$\epsilon/k = T_c\left[\frac{T_c}{\epsilon/k}\right]_{\text{reference gas}} \tag{9}$$

In general Equations (8) and (9) can be applied with excellent results among the group of monatomic gases and among the group of gases tested by Nelson (nitrogen, methane, oxygen, carbon monoxide, and air).

XENON

From the Δ plot for xenon-argon

$$\Delta = 0.93\ T_A$$

and by Equation (7)

$$\epsilon/k]_{Xe} = \epsilon/k]_A\ (1.93) = 230.5°\text{K.}$$

With this value of ϵ/k the xenon temperatures can be reduced to T^*, values of B^* read from the argon plot, and values of b_0 averaged from $T^* = 1.18$ to 1.84 to yield

$$b_0 = 79.96 \text{ cc./g.-mole}$$

As a check by Equation (8) with argon

$$b_0 = \frac{\rho_{c'}b_0]_A}{\rho_{c'}} = \frac{p_c b_0/RT_c]_A}{p_c/RT_c]_{Xe}} = 80.0 \text{ cc./g.-mole}$$

With the force constants in Table 1 the compressibility data of xenon duplicated that of argon within the precision of the data.

METHANE

From the Δ plot for methane-argon

$$\Delta = 4.1 + 0.2375\ T_A$$

and with the same procedures as before

$$\epsilon/k]_{CH_4} = \epsilon/k]_A\left[1.2375 + \frac{4.1}{T_A}\right] = \left[147.76 + \frac{4.1}{T^*}\right]$$

so that

$$\epsilon/k]_{\text{critical}} = 151.0°\text{K.} \quad \epsilon/k]_{\text{Boyle}} = 149.0°\text{K.}$$

The fact that ϵ/k is not a constant shows that methane (and the same is true for nitrogen) does not obey the equation of state dictated by the monatomic gases. Thus to obtain an exact correlation of methane and argon would require variable values for ϵ/k and b_0. From a practical standpoint this is not desirable since it would tend to make the use of the equation of state cumbersome. Also for any gas the variable functions for the force constants are derived from pvT data which must be available over the temperature range in question. Besides, as noted in the previous section, the generalized virial coefficient derivatives showed a good correlation with constant values of b_0 and ϵ/k. Therefore it was decided to assign constant values to the force constants over specified temperature ranges (Table 1) as indicated by accurate reproduction of property data. The methane force constants had first been derived by selecting values of ϵ/k; then an average b_0 was calculated from Equation (4) with the values of dB/dT, and then the mean deviation of the quantity B/b_0 was calculated from the generalized argon B curve. The pair of force constants which gave the minimum deviation were $\epsilon/k = 149.8°$K. and $b_0 = 68.7$ cc./g.-mole. Since these were apparently mean values for the data in the temperature range 0 to 150 deg. and since they correlated the B, C, and virial coefficient derivatives, they were re-

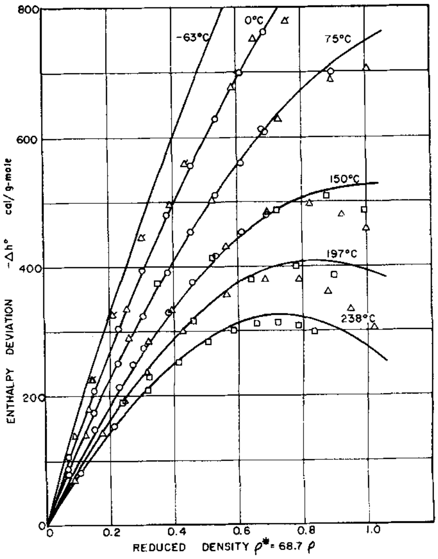

Fig. 3. Methane enthalpy deviation data compared with values calculated from the generalized tables. (Michels: ○), (Tester: △), (Tester's —63°C.: open triangle with slanted dash), (Sage-Lacey: □).

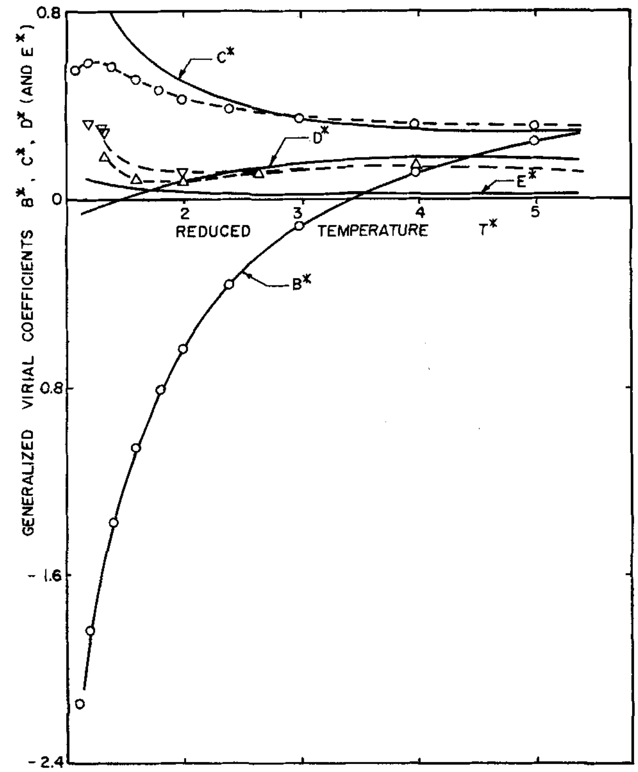

Fig. 4. Comparison of the generalized virial coefficients with theoretical values calculated from the Lennard-Jones potential. (Bird: ○), (Barker-Monaghan: ▽), (Boys-Shavitti: △), (B* or C* or D* or E*: ——).

tained in the construction of the generalized tables. With these values the generalized coefficients reproduce the methane compressibility data within 1% up to $\rho^* = 0.8$ at the highest temperature of the Sage-Lacey (*14*) data (238°C. or $T_r = 2.68$, $p_r = 13.7$, or 627.3 atm.) and up to $\rho^* = 0.45$ at the lowest temperature of the Tester (*15*) data (−63°C. or $T_r = 1.1$, $p_r = 1.33$, or 60.7 atm.).

The compressibility comparisons shown in Figure 2 and the enthalpy deviation comparisons in Figure 3, although specifically for methane, illustrate the general behavior found for all of the gases in Table 1.

NITROGEN

From the Δ plot for ntirogen-argon

$$\Delta = 7.414 - 0.2118\, T_A$$

and by Equation (7)

$$\epsilon/k]_{N_2} = \epsilon/k]_A \left[0.7882 + \frac{7.414}{T_A} \right] = 94.11 + \frac{7.414}{T^*}$$

so that

$$\epsilon/k]_{\text{critical}} = 100.0°\text{K.} \quad \epsilon/k]_{\text{Boyle}} = 96.3°\text{K.}$$

Reliable property data for nitrogen (*14* to *18*) were available to high temperatures (700°K.); hence it was selected as the basic gas for extending the generalized tables to $T^* = 6.0$. To assure that the nitrogen generalized virial coefficients would blend into the argon values the force constant b_0 was calculated by Equation (4) with $\epsilon/k = 96.3$°K. in the temperature range $T^* = 2.83$ to 3.54. This value ($b_0 = 63.6$ cc./g.-mole) was then used to reduce the nitrogen virial coefficients and their derivatives above 0°C. Below 0°C. the nitrogen data are somewhat questionable owing to regions of wide interpolation (*19*). Since nitrogen and methane correlate well on the basis of the modified law of corresponding states, the second set of nitrogen force constants (for low temperatures) were obtained from Equations (8) and (9) with methane as the reference:

$$\epsilon/k]_{N_2} = \frac{\epsilon/k}{T_c}\Big]_{CH_4} \quad T_c]_{N_2} = 99.1°\text{K.}$$

$$b_0]_{N_2} = \frac{\rho_{c'} b_0]_{CH_4}}{\rho_{c'}]_{N_2}} = 62.1 \text{ cc./g.-mole}$$

These values considerably improved the correlation of property data of nitrogen with the generalized tables at temperatures below 0°C.

CARBON MONOXIDE

The force constants are best found by Equations (8) and (9) with nitrogen as the reference:

$$\epsilon/k]_{CO} = 101.4°\text{K.} \quad b_0]_{CO} = 65.1 \text{ cc./g.-mole}$$

Force constants were also derived from Michels' (*20*) two sets of calculated B values by comparison with the B^* tables:

$$\epsilon/k = 100.5°\text{K.} \qquad \epsilon/k = 100.2°\text{K.}$$

$$b_0 = 67.32 \text{ cc./g.-mole} \qquad b_0 = 66.97 \text{ cc./g.-mole}$$

However the constants derived from critical properties were superior to those from Michels' work in predicting property values. It can be surmised from Nelson's (*7*) comments that for temperatures below 0°C. the force constants should be derived from methane, rather than from nitrogen:

$$\epsilon/k]_{CO} = 104.4°\text{K.} \qquad b_0]_{CO} = 63.5 \text{ cc./g.-mole}$$

OXYGEN, AIR, KRYPTON, NEON

The force constants for oxygen (Table 1) above 0°C. were based on nitrogen and below 0°C. on methane to obtain the best fit of compressibility data. Since air should exhibit essentially the same behavior as oxygen, the same procedure was followed for its force constants. In a similar manner the force constants for the monatomic gases, neon, and krypton were established by Equations (8) and (9) with argon as the reference gas.

COMPARISON WITH THE LENNARD-JONES POTENTIAL

The B^*, C^*, D^* virial coefficients of Table 4 are compared with the B^*, C^* virials of Bird-Spotz (*13*) and the D^* virials of Barker and Monaghan (*2*) and of Boys and Shavitt (*3*) in Figure 4. The shape and probable location of the experimental fifth virial is also illustrated.

The second virial (and its derivative) compare very well, but some deviation is apparent at reduced temperatures below 1.6. This small deviation however shows up in calculating the zero-pressure Joule-Thomson coefficients. For example at $T^* = 1.3$ Ishkin and Kagener (*21*) report a value of 1.02 for nitrogen, but from the Bird-Spotz tabulations a value of 0.9833 is obtained and from the tables in this paper, 1.0214. The small difference in B^* is magnified in the C^* difference, with the peak of the experimental C^* values being almost one and one-half times that given by Bird. Kihara (*22*) found that if the bowl of the intermolecular potential function is not wide enough, the theoretical C virial will be too small. He concludes that the real potential for rare gases has a wider bowl and a harder repulsive wall than the Lennard-Jones 6-12 potential. Too, the third virial coefficients of Table 4 compare favorably with the results of other investigators (*19*). From Table 3 it can be deduced that the inclusion of the

Table 2. Pressure and Density Limits for Evaluation of Compressibility Factors

Temperature	T^*	5.5	4.0	3.0	2.5	2.0	1.4
Suggested	ρ^*	0.90	0.87	0.74	0.67	0.55	0.37
Limit	p^*	7.97	5.05	2.60	1.69	0.90	0.31

Table 3. Mean Error in Calculated Δh° for Different Investigators
(Units are cal./g.-mole)

Gas	Michels	Din	Tester	Sage-Lacey
N_2	1.7	3.4		4.8
CH_4	2.6		9.6	7.6
A	1.6	14.7		
Xe	3.7			
Overall mean error	2.2	10.9	9.6	6.2
$\Delta h^\circ/R(\epsilon/k)$	(0.00788)	(0.04715)	(0.03246)	(0.02563)

Table 4*

Generalized second virial coefficient and derivatives

T^*	B^*	dB^*/dT^*	d^2B^*/dT^{*2}
6.0	0.317	0.064	-0.022
5.0	0.239	0.094	-0.045
4.0	0.115	0.163	-0.096
3.0	-0.114	0.317	-0.247
2.0	-0.625	0.816	-0.933
1.20	-1.870	2.949	-6.207

Generalized third virial coefficient and derivatives

T^*	C^*	dC^*/dT^*	d^2C^*/dT^{*2}
6.0	0.284	-0.008	0.001
5.0	0.293	-0.010	0.003
4.0	0.306	-0.019	0.026
3.0	0.349	-0.079	0.095
2.0	0.502	-0.280	0.409
1.20	0.928	-0.429	-6.000

Generalized fourth virial coefficient and derivatives

T^*	$D^{*\dagger}$	dD^*/dT^*	d^2D^*/dT^{*2}
6.0	0.137	-0.018	-0.003
5.0	0.153	-0.014	-0.006
4.0	0.161	0.002	-0.030
3.0	0.138	0.047	-0.058
2.0	0.060	0.115	-0.084
1.2	-0.063	0.199	-0.129

* Complete tables are available without charge from the authors.
† Add 0.02 to D^* values for monatomic gases.

experimental D^* allows an average increase in the maximum density by a factor of 2.8 over the Bird-Spotz limit.

Both of the theoretical calculations (Lennard-Jones model) of D^* disclose the same peculiarities, a maximum near $T^* = 4.0$ and a minimum near $T^* = 2.0$. In this range the values essentially agree with the experimental values. Below $T^* = 2.0$ the graphs differ from the experimental curve, which is a continuously decreasing function. Boys and Shavitt state that the calculational errors are magnified at low temperatures, although Barker and Monaghan feel that their values are quite reliable. The authors feel that the theoretical values are in error for two reasons. (*a*) With these values at a given density compressibility data are given more accurately at low temperatures than at higher temperatures, an unusual result since to fit property data to the same density requires more virial coefficients at the lower rather than at the higher temperature. For example with Bird's B^*, C^*, and Barker's D^* at a temperature of $T^* = 1.4$

ρ^*	0.2	0.4	0.6	0.8	1.0
$z - z$ calc	0.004	0.016	0.030	0.014	-0.017

These results illustrate that the theoretical coefficients will either fit the data to a high density or cross over the experimental isotherm plot. Both alternatives are doubtful, especially the latter, since then E^* must of necessity be negative, which is not indicated by the experimental properties. (*b*) The Lennard-Jones 12-6 potential is not an exact representation of the intermolecular potential, and the deviations from the experimental virial coefficients will increase with the higher virials and lower temperatures.

The shape and probable location of the experimental fifth virial coefficient is also illustrated in Figure 4. A large number of experimental internal energy and compressibility isotherms were considered to establish the sign and relative magnitudes of E^* and dE^*/dT^*. Negative slopes are dictated from the internal energy deviation data, while small positive values of E^*, decreasing with increasing temperature, are dictated by compressibility data.

From Figure 4 it can be concluded that the experimental B^*, D^*, and perhaps F^*, etc. will be similar in shape and likewise C^*, E^*, etc.

ACCURACY

To assign an absolute measure of accuracy to the generalized virial tables is impossible if only because of the disagreement in the property values proposed by different investigators. A study of compressibility data dictated the density and pressure limits in Table 2. A mean error in z of only 0.001 is estimated within the suggested density limits (that is within the precision of the experimental data).

Comparison of experimental and calculated Δu^o and Δh^o values were made at arbitrary states within the suggested density limits. The comparisons were further restricted to the temperature ranges wherein the property data had been adjudged accurate (*19*). To explain, some regions were noted where the property data were somewhat questionable. Usually this was due to a lack of and wide spacing of experimental data so that interpolation was necessary on the part of the different investigators. Although the compressibility data of various investigators generally correlate well, the calculated property values show a greater variation and in some cases a very definite disagreement [for example the low temperature Δh^o values for methane of Tester (*15*), Figure 3]. The mean errors or differences in Δh^o calculated from Table 4 vs. the values for various sources are listed in Table 3. Error in extrapolating experimental zero-pressure enthalpy values to calculate Δh^o could account for the relatively large difference found for Din's argon results, which might reduce the 14.7 values by 2 or 3 cal./g.-mole. The deviation from Tester's methane Δh^o can be reduced to 6 cal./g.-mole if the low-temperature (210°K.) isotherm is ignored. Over the range of densities indicated in Table 2 it appears that a mean error in Δh^o of 2 to 6 cal./g.-mole can be assumed between the specific data and the values calculated from the generalized tables. It is felt that Michels' data are more reliable, which would indicate a mean error in Δh^o of only 2 to 3 cal./g.-mole for Table 4. The mean error between Table 4 and Michels' Δu^o is also approximately 2 cal./g.-mole, indicating again that the error in compressibility is small and that Table 4 yields rather precise property data.

Typical correlation results are shown in Figures 5 and 6 which also show the predictions of the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state [with the constants of Benedict (*24*)]. From a study of zero-pressure Joule-Thomson coefficients the authors be-

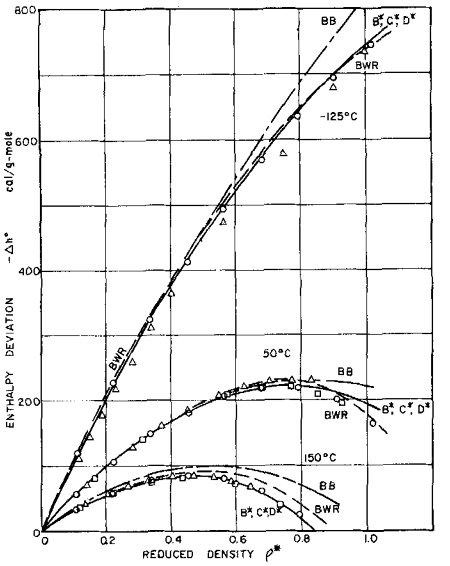

Fig. 5. Nitrogen enthalpy deviation data compared with values calculated from the generalized tables and with equations of state. (Michels: ○), (Din: △), (Sage-Lacey: □), (Beattie-Bridgeman equation: BB), (Benedict-Webb-Rubin equation: BWR), (B^*, C^*, D^*: ——).

lieve the Sage-Lacey 238 deg. values in Figure 6 are in error and that the generalized curve is closer to the truth. Also reduction of the nitrogen Δh^o and the Sage-Lacey isotherm with the force constants ϵ/k and b_0 in the form $\Delta h^o/R$ (ϵ/k) vs. ρ^* indicates that the methane values should be increased slightly to correlate the nitrogen points.

The ability of the generalized tables to predict the zero-pressure Joule-Thomson coefficients is illustrated in Figure 7.

A rather severe test of an equation of state is its ability to predict the velocity of sound. Figure 8 illustrates Itterbeek's data (25) for nitrogen and the values calculated from Table 4.

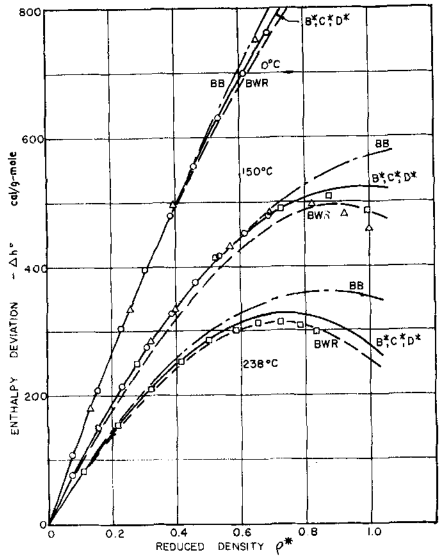

Fig. 6. Methane enthalpy deviation data compared with values calculated from the generalized tables and from equations of state. (Michels: ○), (Tester: △), (Sage-Lacey: □), (Beattie-Bridgeman equation: BB), Benedict-Webb-Rubin equation: BWR), (B^*, C^*, D^*: ——).

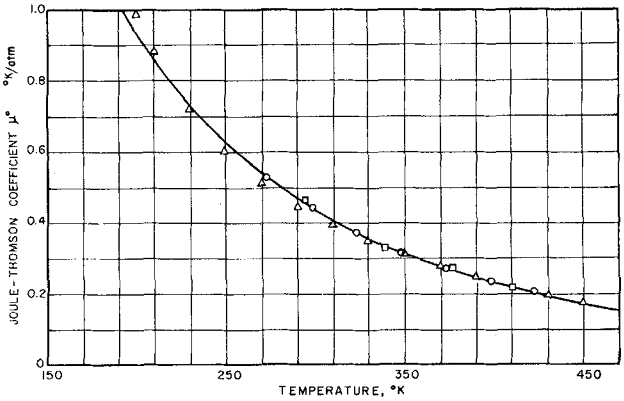

Fig. 7. Zero-pressure Joule-Thomson coefficients for methane compared with values calculated from the generalized tables. (Michels: ○), (Tester: △), (Sage-Lacey: □), (B^*, C^*, D^*: ——).

CONCLUSIONS

The generalized virial coefficients and their derivatives presented in this paper are believed to be more accurate than other such tables, and more accurate than most equations of state, within the prescribed density limits and for the simpler, nonpolar gases. The conclusive test of the virial equation was its ability to predict accurately not only experimental pvT data but also other properties such as Δu^o and Δh^o by satisfying the temperature derivatives of the virial coefficients. Since the tables rest upon a principle of corresponding states which has been well tested, the tables may be used as a guide in the selection of future theoretical potential functions and to test or to better align experimental data.

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NOTATION

b_0 = empirical reduction constant
B, C, D = virial coefficients (temperature functions)
h = enthalpy ($\Delta h^o = h - h_{\text{ideal}}$)
p = pressure
R = universal gas constant

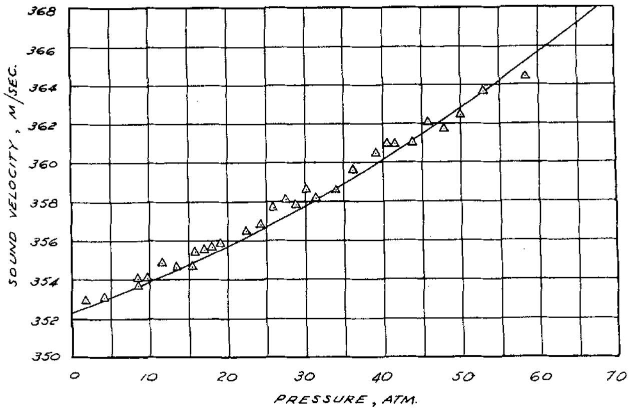

Fig. 8. Velocity of sound for nitrogen at 298.72°K. (van Itterbeek: △), (B^*, C^*, D^*: ——).

T = absolute temperature
u = internal energy ($\Delta u^o = u - u_{\text{ideal}}$)
z = compressibility factor ($z = pv/RT$)

Greek Letters

Δ = temperature difference between argon and selected gas at z minimum
ϵ/k = empirical reduction constant
ρ = density
$\rho_{c'}$ = pseudo-critical density ($\rho_{c'} = p_c/RT_c$)
μ^o = Joule-Thomson coefficient at zero pressure

Superscript

$*$ = reduced or generalized values

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Velocity Distributions in Two-Dimensional Laminar Liquid-into-Liquid Jets in Power-Law Fluids

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The study of boundary-layer equations for non-Newtonian fluids has lately become of interest. It has been shown (*1, 4, 7, 11, 14, 15*) that these equations become mathematically treatable (*15*) for the simplified case of the so-called *power-law* fluid. Numerical solutions have been published for a boundary layer near a flat plate (*1*). In this paper the flow behavior of a two-dimensional laminar liquid-into-liquid jet will be investigated, and complete analytical solutions will be presented.

The case of the two-dimensional jet is important in the study of the laminar mixing of non-Newtonian fluids as it represents a simple model of the entrainment process. Furthermore the fact that the solution is analytical is of special value in investigating the general properties of boundary-layer equations in non-Newtonian fluids.

THE BOUNDARY-LAYER EQUATIONS FOR A NON-NEWTONIAN FLUID

The general equation for steady state two-dimensional flow of an incompressible liquid can be written as

$$\rho u_j \frac{\partial u_i}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_j} \qquad (1)$$

Rivlin and Ericksen (*9, 10*) have shown that for any isotropic incompressible fluid with no memory the stress tensor τ_{ij} can be defined as a polynomial function of the kinematic matrices. In cases where only the first- and second-order matrices are required to define τ_{ij}

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