form particle size of the solid solute, a precisely controlled heating rate, and a reproducible initial state for the heating runs.

While the present argument is in terms of overshoot temperature and heating rate, which requires a knowledge of the static temperature of saturation, in general, it would not be necessary to know the static temperature to apply the method—that is, the saturation temperature at the zero heating rate could similarly be obtained by extrapolating the dynamic solubility temperatures, directly, rather than the overshoot.

The present method bears a clear resemblance to the corrective procedure for eliminating the effect of supercooling on freezing point measurements. There a time-temperature plot is extrapolated through the region of supercooling back to a temperature corresponding to the onset of crystallization. In the present situation a time-related function–solubility temperature plot is extrapolated through the region of superheating (the overshoot) to the temperature onset of homogeneity. The time-related function is the heating rate.

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Nitrogen Constants for the Benedict-Webb-Rubin Equation of State

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A new set of Benedict-Webb-Rubin constants for nitrogen is presented. These constants were developed to represent gas phase *P-V-T* behavior over the full BWR density range to twice the critical, in the temperature range below 373° K. The over-all accuracy is very satisfactory, especially in the higher density region, where the earlier constants of Stottler and Benedict are not applicable. Accuracy of the constants in representing wide-range mixture data also has been demonstrated, using previously published argon constants and combining rules, and recent Ar–N_2 *P-V-T* data.

THE Benedict-Webb-Rubin equation of state (*3, 4*) was developed originally to represent the behavior of light hydrocarbons and their mixtures to twice the critical density. The equation subsequently has been applied to a number of other substances (*9, 11, 13, 14*). As has been discussed elsewhere (*9*), it is not possible to determine a unique set of constants for this equation that will correlate accurately liquid-vapor phase behavior as well as gas phase *P-V-T* behavior over a wide range of temperature and pressure. Several solutions to this problem have been proposed in these references: One or more of the coefficients are varied for use in the different regions of the *P-V-T* surface; various modifications in the functional representation are utilized; individual sets of constants are developed, one based on vapor pressure data and another on gas phase *P-V-T* data.

Currently, two sets of nitrogen constants are available for the BWR equation. Stottler and Benedict (*13*), using the originally proposed graphical technique, fit the equation to *P-V-T* data for a maximum density of 1.25 ρ_c. To improve vapor pressure correlation, they adjusted the constant C_0 at two temperatures. Lin and Naphtali (*9*) have presented a set of nitrogen constants determined from vapor pressure data by means of a least squares technique. In addition, they modified one temperature exponent in the equation.

It would be desirable to have available a set of nitrogen constants for the unmodified equation that represent *P-V-T* behavior over the full density range of the equation. Such constants, in addition to increasing the range of applicability for nitrogen calculations, would be especially useful in correlating wide-range mixture data, and also for phase equilibria correlations not requiring nitrogen vapor-pressure prediction (*12*). The constants from (*13*) are not applicable above 1.25 ρ_c, and for temperatures below about 200° K., begin to give appreciable errors above 1.0 ρ_c. The other set (*9*), intended for *K*-factor prediction, are not suitable for wide-range *P-V-T* calculations.

EVALUATION OF THE CONSTANTS

For the reasons discussed above, a new set of nitrogen constants was developed for the unmodified BWR equation of state, covering the full density range shown in Figure 1. The experimental *P-V-T* data used in the final evaluation (*1, 2, 5, 6, 7, 10*) are shown on the plot, and include recent low temperature data. The range is 100° to 373° K., and from low density to 2.0 ρ_c (to saturated vapor below T_c).

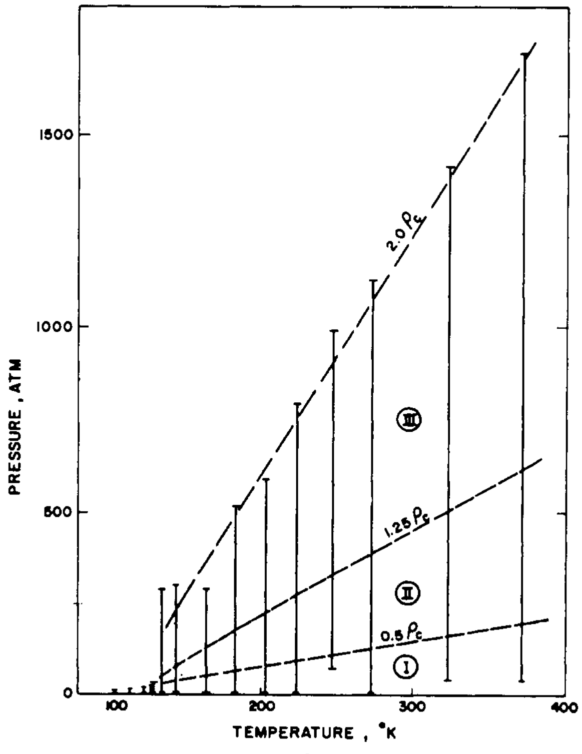

Figure 1. Range of experimental data

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The constants were determined using a linear stepwise regression technique and a digital computer. Such a technique involves minimization in standard deviation of the dependent variable, which may conveniently be either $(Z - 1)$ or $(P - RT\rho)$. Both procedures were followed in this investigation, and the resulting constants and accuracy of fit were surprisingly close. The results presented here are those determined using $(Z - 1)$ as the dependent variable. The BWR equation in terms of compressibility factor is

$$Z = 1 + (B_0 - A_0/RT - C_0/RT^3)\rho + (b - a/RT)\rho^2 + a\alpha\rho^5/RT + (c\rho^2/RT^3)\,(1 - \gamma\rho^2)\ \text{exptl.}\ (-\gamma\rho^2)$$

The value for R was taken to be consistent with the majority of other substances for which BWR constants from *P-V-T* data are available.

Because of the nonlinear exponential term in the equation, it was necessary to assume various values for γ until a minimum in standard deviation of the dependent variable was reached. The value of γ at this minimum point and the corresponding coefficients for that γ from the regression program were then considered to be the best values for the eight BWR constants, which are presented in Table I. No attempt was made to adjust constants at low temperature for improved vapor pressure correlation; the constants from (*9*) were developed specifically for that purpose.

EVALUATION OF THE FIT

The standard deviation in $(Z - 1)$ for the 321 data points considered in the final evaluation is 0.00674. Perhaps a more meaningful indication of the accuracy is the average absolute per cent error in Z, given in Table II for the entire range of data, and also for the three density ranges indicated in Figure 1. As might be anticipated, the new constants are somewhat less accurate than those from (*13*) in the low and moderate density regions, I and II, but are nevertheless felt to give a satisfactory representation. In the high density region III, the new constants are very good, while those from (*13*), not being intended for this range, are strictly unsuitable.

A point by point comparison of the calculated and experimental values also yields important information regarding the nature of the fit. The principal contributions to the average error in both regions II and III occur in the immediate vicinity of the critical point. For example, eliminating two high density points at the critical temperature (about 7% deviation) reduces the average deviation for region III significantly, from 0.75% to 0.55%. Similarly, the error in region I is associated primarily with the higher temperature range. The fit could be improved in either or both of these small regions, but only at the expense of other regions or the over-all accuracy. The constants presented in Table I are those considered to be the best compromise.

Table I. BWR Constants for Nitrogen

B_0 = 0.0281066
A_0 = 0.872086
C_0 = 7813.75
b = 0.0032351
a = 0.0312319
α = 0.0000709232
c = 547.364
γ = 0.0045

Units: atm., l./gram-mole, ° K., R = 0.08207

Table II. Average Absolute Per Cent Error in Z for Nitrogen

Density Range	No. of Points	Nitrogen Constants, %	
		This work	Ref. (*13*)
I, II, III (over-all)	321	0.47	3.0
I (low)	167	0.23	0.13
II (medium)	87	0.69	0.34
III (high)	67	0.75	13.53

Table III. BWR Constants for Argon (*14*)

B_0 = 0.0222825
A_0 = 0.823408
C_0 = 13141.1
b = 0.00215287
a = 0.0288353
α = 0.0000355884
c = 798.231
γ = 0.0023

Units: atm., l./gram-mole, ° K., R = 0.08207

Table IV. Average Absolute Per Cent Error in Z for Mixtures[a]

Nominal Composition	No. of Points	Nitrogen Constants, %	
		This work	Ref. (*13*)
100% Ar	78	0.61	0.61
80% Ar-20% N_2	84	0.62	1.35
50% Ar-50% N_2	90	0.79	4.41
20% Ar-80% N_2	90	0.58	3.48
100% N_2	90	0.43	2.74

[a] Data from Ref. (*6*).

APPLICATION TO MIXTURE BEHAVIOR

Application of the BWR equation of state to wide-range mixture *P-V-T* behavior was one of the principal factors leading to the development of the new nitrogen constants. The equation was tested against experimental data (*6*) for argon, nitrogen, and their mixtures, covering the temperature range 143° to 273° K. and maximum densities of approximately twice the critical.

The argon constants (*14*) used in this investigation are listed in Table III. The mixture combining rules (*8*) used are as follows: a Lorentz combination for B_0; linear square-root combinations for A_0, C_0, and γ; and linear cube root combinations for a, b, c, and α.

The results, presented in Table IV, are felt to be very satisfactory. The average errors in Table IV associated with the use of nitrogen constants from (*13*) result primarily from those points above the critical density.

CONCLUSIONS

As is the case with any high density equation, the use of the Benedict-Webb-Rubin constants for nitrogen presented in this paper must necessarily involve somewhat of a compromise in low to moderate density correlation. However, the advantages gained through extension of the range of applicability of this equation (to include all three regions of Figure 1) should be sufficient to warrant their use in a number of applications.

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NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = Benedict-Webb-Rubin constants
P = pressure
R = gas constant
T = temperature
Z = compressibility factor
ρ = density
ρ_c = critical density

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Thermodynamic Functions for 1,2-Dichloro-1,1-difluoroethane

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Thermodynamic functions C_p°, S_t°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ have been computed for 1,2-dichloro-1,1-difluoroethane in the ideal gas state from 250° to 750° K. at 1 atm. pressure. The restricted internal rotational contribution has been treated in two ways: by the Lielmezs-Bondi approximate method and the conventional treatment of Pitzer and Gwinn. The agreement between the calculated results by both methods is satisfactory.

THE RECENT availability of spectroscopic data for 1,2-dichloro-1,1-difluoroethane (*1, 5, 8*) has made it possible to estimate the thermodynamic functions—heat capacity, enthalpy, entropy, and free energy—for the equilibrium mixture of trans and skew form isomers of this compound in the ideal gas state at 1 atm. pressure. Table I gives the thermodynamic functions calculated by both the Lielmezs-Bondi approximate method (*3, 7, 9, 10*) and the Pitzer and Gwinn (*11, 12*) method corrected for the asymmetrical top contribution (*4*).

To compute the tabulated thermodynamic function values, a digital computer (IBM-7040) program has been coded (*3*) evaluating the reduced moment of inertia (Equation 1), the two Pitzer and Gwinn parameters, V_0/RT and $1/Q_f$,

$$Q_f = \frac{2.7935}{n_m}\,(I_{\text{red}}10^{38}T)^{1/2},$$

Table I. 1,2-Dichloro-1,1-difluoroethane Thermodynamic Functions

Temperature,	C_p° Cal./Mole – °K.		S_t°, E.U.		$(H^\circ - H_0^\circ)/T$ Cal./Mole – °K.		$-(F^\circ - H_0^\circ)/T$ Cal./Mole – °K.	
°K.	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]
250	21.32	...	79.70	...	14.96	...	64.74	...
298.15	23.40	...	83.64	...	16.16	...	67.48	...
350	25.47	25.25	87.56	87.64	17.39	16.74	70.16	70.91
400	27.25	27.10	91.08	91.14	18.52	17.92	72.56	73.22
450	28.81	28.72	94.38	94.43	19.58	19.03	74.80	75.40
500	30.18	30.13	97.49	97.53	20.57	20.07	76.92	77.46
550	31.36	31.36	100.43	100.46	21.50	21.04	78.92	79.42
600	32.40	32.44	103.20	103.24	22.37	21.95	80.83	81.29
650	33.31	33.38	105.83	105.87	23.18	22.79	82.65	83.08
700	34.12	34.22	108.33	108.38	23.93	23.58	84.40	84.79
750	34.83	34.96	110.71	110.76	24.64	24.31	86.08	86.45

[a] L-B, Lielmezs-Bondi approximate method (*9, 10*). [b] P-G, Pitzer and Gwinn tables (*11, 12*) corrected for asymmetrical top contribution (*4*).

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