An Improved Generalized Equation of State

Two forms of a generalized Benedict-Webb-Rubin Equation, BWR24 and BWR44, are proposed for dense gases which represent an improvement by a factor of about three in calculated pressures compared to reduced forms of this relationship in the literature. The method is also tested for accuracy in predicting enthalpy departures for pure components and mixtures. The proposed methods are marginally better than the best of other methods tested. Major advantages for the proposed equations are their relative simplicity, low computer storage requirements, and generality. No mixture interaction constants are required other than those already available in the literature.

TOMOYOSHI YAMADA

Department of Chemical Engineering
University of Wyoming
Laramie, Wyoming 82070

SCOPE

Process design and simulation requires extensive use of thermodynamic data. Computerization of such calculations has made use of complicated equations of state practical and frequently necessary for greatest accuracy. Even when experimental data are available, an accurate equation of state may minimize computer storage requirements through the elimination of extensive tables and table look-up procedures.

A generalized equation of state is a necessity if experimental data are lacking or must be extrapolated over wide ranges of temperature, pressure, and composition. In contrast to nongeneralized equations, a generalized relationship in the form of a three parameter corresponding states correlation may be used even when no volumetric (PVT) data exist for a compound except for the critical temperature, the critical volume (or pressure) and a vapor pressure from which the acentric factor (Pitzer and Curl, 1957) is calculated.

The equation of state of Benedict, Webb, and Rubin (1940) is one of the best and one of the most widely used, and various attempts have been made to generalize this equation (Edmister et al., 1968; Opfell et al., 1956; Su and Viswanath, 1965).

In using an empirical equation of state, the method of curve fitting the equation constants is extremely important. In this work substantially improved accuracy for the generalized BWR Equation is achieved by altering the curve fitting procedures usually adopted.

CONCLUSIONS AND SIGNIFICANCE

Two equations of state are proposed. BWR24 with 24 coefficients is restricted to reduced densities less than 1.8 whereas BWR44 with 44 coefficients gives good results even at reduced densities as high as 2.8. A carefully selected procedure is used to determine the coefficients for these equations, and an improvement by almost a factor of three is achieved in the accuracy of predicted pressures as compared to previous generalized forms of the BWR.

For 16 nonpolar gases the average deviation between calculated and experimental pressures is ½% for both proposed equations within the specified density ranges. Enthalpy departures for fourteen mixtures and five pure components are predicted with an average deviation from the experimental values of about four joules/g. The proposed equations are tested for vapors and dense gases but not for liquids.

Major advantages for the proposed equations are: (1) Relative simplicity when compared with the most accurate methods currently available. (2) The equations are readily applicable to nonpolar gaseous mixtures. No mixture interaction parameters are required other than those already available in the literature.

GENERALIZATION OF THE BWR EQUATION

The reduced form of the BWR Equation used here is identical with that used previously by Edmister et al. (1968).

$$Z = 1 + \left(B_{OR} - \frac{A_{OR}}{T_R} - \frac{C_{OR}}{T_R^3}\right)\frac{1}{V_R} + \left(a_R - \frac{b_R}{T_R}\right)\frac{1}{V_R^2} + \frac{\alpha_R}{V_R^5 T_R} + \frac{c_R}{T_R^3 V_R^2}\left(1 + \frac{\gamma_R}{V_R^2}\right)\exp\left(-\frac{\gamma_R}{V_R^2}\right) \quad (1)$$

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866\omega} \quad (2)$$

The eight coefficients, B_{OR}, A_{OR}, etc., are assumed to be

Correspondence concerning this paper should be addressed to R. D. Gunn, College of Engineering, University of Wyoming, Laramie, Wyoming 82070.

quadratic functions of the acentric factor and are listed in Table 2a. Parameters used in this work are listed in Table 1.

V_{sc}, the scaling volume, is used as a scaling factor because it is found to lead to more accurate results than the critical volume which is subject to large experimental errors. If liquid density data are not available at a reduced temperature of 0.6, the scaling volume can be calculated from equations given by Gunn and Yamada (1971). This reference also lists V_{sc} for 32 compounds. Because V_{sc} is measured far from the critical point, it can be calculated to within about 0.25% in most cases.

Previous investigators have usually developed a generalized BWR Equation from the constants for the individual gases. These BWR coefficients unfortunately are functions of the temperature and pressure range for the experimental data used in the least squares fitting process. This temperature and pressure dependence of the individual coefficients leads to error in the final corresponding states correlation. Therefore, in order to produce an improved generalized equation of state, the following procedures are adopted in the calculation of the constants for BWR24:

1. The reduced constants are determined from several gases simultaneously with PVT data covering a very wide range of reduced temperatures, pressures, and acentric factors.
2. BWR24 is limited to a maximum reduced density of 1.8 because any attempt to fit the equation to substantially higher densities leads to greatly decreased accuracy at lower pressures.
3. As a reducing parameter the scaling volume is used because it is known more accurately than the critical volume. V_{sc} is also believed to be somewhat more accurate than the ratio RT_c/P_c.

The 24 coefficients listed in Table 2a are determined by a least squares method from 987 experimental data points for the compounds: argon, methane, ethane, *n*-butane, *n*-pentane, *n*-heptane, and nitrogen. These data points cover a very wide range of conditions: 0.8 to 5.5 in the reduced temperature and 0 to 1.8 in the reduced density. The proposed equation is referred to as BWR24 hereafter.

Table 1. Critical Properties and Acentric Factors Used in this Study

Substance	Tc K	Vsc, cm³/g-mole	ω
Argon	150.72	75.24	.000
Carbon dioxide	304.19	93.55	.225
Nitrogen	126.2	89.64	.040
Hydrogen sulfide	373.4	97.53	.100
Methane	190.55	99.53	.013
Ethane	305.43	145.42	.099*
Propane	369.82	199.79	.153*
n-butane	425.16	254.07	.201*
iso-butane	408.13	256.72	.185*
n-pentane	469.6	310.97	.253*
iso-pentane	460.39	308.17	.229*
neo-pentane	433.75	311.09	.197*
n-Hexane	507.4	368.48	.294*
n-heptane	540.2	429.28	.350*
Ethylene	282.36	130.41	.088*
Propylene	365.0	183.02	.143*
Benzene	562.09	255.53	.215

* From vapor pressure of Project 44 and T_c and P_c from Kudchadker et al. (1968).

Table 2a. Coefficients in BWR24

$$B_{OR} = 0.39911 + 0.59024\omega - 2.89764\omega^2$$
$$A_{OR} = 1.14847 + 0.39761\omega - 6.66115\omega^2$$
$$C_{OR} = 0.39050 + 0.87856\omega + 3.38459\omega^2$$
$$b_R = 0.31077 + 1.94019\omega - 1.27801\omega^2$$
$$a_R = 0.24505 + 3.50431\omega - 0.77333\omega^2$$
$$c_R = 0.36622 + 2.30309\omega - 0.10514\omega^2$$
$$\alpha_R = 0.03707 + 0.14000\omega - 0.07786\omega^2$$
$$\gamma_R = 0.60200 - 0.35000\omega + 0.02500\omega^2$$

Table 2b. Coefficients in BWR44

$$B_0 = 0.433757 - 3.246378\omega$$
$$B_1 = -0.862937 + 9.939630\omega$$
$$B_2 = -0.756530 - 8.293955\omega$$
$$B_3 = 0.027745 + 0.917885\omega$$
$$C_0 = 0.094959 + 8.236604\omega - 21.016663\omega^2$$
$$C_1 = 0.109501 - 12.094533\omega + 31.417587\omega^2$$
$$C_2 = -0.122534 + 2.069143\omega - 4.935475\omega^2$$
$$C_3 = 0.382121 + 3.329449\omega - 6.299470\omega^2$$
$$C_4 = 0.602403 + 0.479766\omega - 2.358322\omega^2$$
$$D_0 = 0.043682 - 5.572401\omega + 14.261955\omega^2$$
$$D_1 = -0.056852 + 2.793468\omega - 9.629090\omega^2$$
$$E_0 = 0.010344 + 2.942841\omega - 6.694306\omega^2$$
$$E_1 = 0.004545 - 0.024887\omega + 0.189640\omega^2$$
$$E_2 = 1.2004 + 3.744705\omega - 5.568792\omega^2$$
$$F_0 = 0.002304 - 0.764692\omega + 1.742159\omega^2$$
$$F_1 = 0.029587 + 0.182171\omega - 0.261855\omega^2$$

EVALUATION

Deviations between calculated and observed pressures for 16 compounds below a reduced density of 1.8 are shown in Table 3 for BWR24. This table also includes deviations for several other equations: The generalized BWR of Edmister et al. (1968); the BWR with the original coefficients (Benedict et al., 1940); Sugie and Lu (1970, 1971); Barner and Adler (1970); and BWR44 which will be discussed later. Grand average deviation for BWR24 is 0.48% in the calculated pressure. This is almost three times better than the best of the other generalized BWR Equations. It is also better than the original non-generalized BWR Equation which has an average absolute deviation of 0.65% in the same region examined.

Superficially this last result is surprising because constants for the original equation were obtained by a least squares procedure for each component separately. A single set of generalized parameters normally is not expected to produce greater accuracy than the individual constants. However, an empirical equation of state such as the BWR cannot be extrapolated safely beyond the region in which the parameters are determined. The original constants in the BWR equation were calculated from a very narrow range of data for several compounds, and predictive accuracy is poor outside of this range. In contrast the generalized equation presented here is valid over a very wide range of temperatures and pressures.

This principle is clearly demonstrated in Table 4 for ethane at 327°K. The original constants for the BWR equation were calculated only from data at reduced densities below 1.5. Above this density the original BWR coefficients give poor predictions for ethane.

After completion of the present work a new generalized BWR equation was reported by Starling and Han (1972). These authors report an average deviation of 1.26% in calculated densities for 14 substances and 659 data points including some in the liquid phase. For the same compounds BWR24 shows an average deviation of 0.47% for

1137 data points. This comparison obviously is not based on identical data sets.

An important difference between Equation (1) and the generalized BWR presented by Starling and Han is that the latter is linear in the acentric factor. Analyses made in this work indicate that a correction term which is second order with respect to the acentric factor is statistically significant. This is not unexpected. If the compressibility factor Z is a function of the reduced pressure at constant temperature and is linear with respect to the acentric factor, then higher order terms in the acentric factor arise naturally if the equation for Z is transformed to reduced density as an independent variable.

The scaling volume and the critical volume are nearly identical numerically in many instances, and either may be used as a reducing parameter. Sometimes, however, the use of the scaling volume greatly improves the predictive accuracy of Equation (1). Starling and Han (1972), for example, record an average deviation of 2.63% in predicted densities for ethylene which is the largest deviation reported for any nonpolar gas. In contrast an average deviation of only 0.35% is observed for ethylene densities calculated from Equation (1). The greatly improved accuracy for ethylene in this work is believed to result primarily from the use of a scaling volume which is about 5% larger than the critical volume used by Starling and

TABLE 3. COMPARISON OF EQUATIONS OF STATE BELOW A REDUCED DENSITY OF 1.8

Substance	T_R	Max. density (reduced)	No. of pts.	Avg. abs. dev. in pressure, %* Methods 1	2	3	4	5	6	Data source
Argon	0.78-1.65	1.78	205	0.91	—	2.94	0.63	0.41	0.21	Michels et al. (1958)
Methane	1.06-2.48	1.75	107	2.65	0.31	1.33	0.34	0.28	0.22	Kvalnes and Gaddy (1931)
Ethane	1.02-1.62	1.77	129	3.88	0.81	1.31	0.57	0.37	0.26	Sage and Lacey (1950)
Propane	0.84-1.38	1.77	111	2.79	0.36	1.28	0.62	0.31	0.29	Sage and Lacey (1950)
Propane	1.00-1.48	1.80	130	3.02	0.39	1.67	0.92	0.44	0.33	Beattie et al. (1937)
n-butane	0.89-1.20	1.74	98	1.49	0.37	1.15	0.43	0.25	0.29	Sage and Lacey (1950)
iso-butane	1.04-1.40	1.80	106	2.24	1.06	2.24	0.64	0.53	0.81	Beattie et al. (1950)
n-pentane	1.00-1.22	1.55	45	0.71	1.76	0.76	0.79	0.39	0.37	Beattie et al. (1952)
neo-pentane	1.00-1.26	1.55	54	0.79	—	1.95	0.88	0.72	0.89	Beattie et al. (1952)
n-hexane	1.03-1.08	1.65	48	3.32	1.03	2.15	2.52	1.15	1.17	Griskey and Canjar (1959)
n-hexane	1.01-1.13	1.66	10	3.40	0.74	1.42	2.42	0.55	0.47	Kelso and Felsing (1940)
n-heptane	1.01-1.15	1.71	28	1.79	0.39	1.79	0.98	0.67	0.60	Smith et al. (1937)
Ethylene	0.97-1.50	1.74	64	2.94	0.13	0.30	0.70	0.41	0.54	Din (1959)
Propylene	0.82-1.16	1.75	54	1.72	0.87	1.26	0.46	0.24	0.32	Michels et al. (1953)
Benzene	0.91-1.12	1.30	139	0.93	0.37	0.54	0.66	0.43	0.40	Gornowski et al. (1947)
Nitrogen	1.35-5.54	1.55	57	1.86	—	0.77	0.25	0.62	0.28	Din (1959)
Carbon dioxide	0.90-1.39	1.78	151	1.23	—	0.84	0.33	0.53	0.34	Din (1959)
Hydrogen sulfide	0.74-1.19	1.79	60	1.93	0.34	0.61	0.43	0.42	0.48	Sage and Lacey (1955)
Grand. Avg. Dev.			1596	2.09	0.65	1.35	0.81	0.48	0.46	

* % Dev. = $100(P_{EXP} - P_{CALC})/P_{EXP}$.
Methods: 1. Barner-Adler (1970).
2. Original BWR Equation.
3. Generalized BWR Equation of Edmister et al. (1968).
4. Sugie and Lu (1970, 1971).
5. BWR24.
6. BWR44.

TABLE 4. THE 328K ISOTHERM FOR ETHANE
Data source: Sage and Lacey (1950)

ρR Vsc/V	P_{EXP} [atm]	Z_{EXP}	% Dev. in calculated pressure Original BWR	Generalized BWR	BWR24	Sugie and Lu	BWR44
0.0800	13.61	0.9206	−0.26	−0.12	−0.04	−0.27	−0.14
0.1773	27.22	0.8306	−0.49	−0.14	0.00	−0.38	−0.13
0.3053	40.83	0.7234	−0.59	0.06	0.21	−0.18	0.08
0.5042	54.44	0.5841	−0.33	0.87	0.80	0.75	0.59
0.8794	68.05	0.4186	−0.35	1.90	0.43	0.55	0.04
1.4923	102.07	0.3700	−0.48	0.30	0.12	2.89	0.98
1.6592	136.09	0.4437	−3.06	−3.38	−1.36	2.21	−0.56
1.7648	170.11	0.5215	−3.00	−3.87	−0.63	2.20	−0.51
1.8357	204.14	0.6016	−3.80	−4.93	−1.13	0.55	−1.78
1.9559	272.18	0.7528	0.27	−1.15	3.35	2.16	0.81
2.0327	340.23	0.9055	0.53	−0.94	3.60	0.20	−0.37
2.1529	476.32	1.1969	3.43	1.97	6.34	−0.75	−0.26
2.2861	680.46	1.6103	8.64	7.25	11.18	0.03	1.23
Avg. dev. $\rho_R < 1.8$			1.07	1.33	0.45	1.18	0.38
Avg. dev. $1.8 < \rho_R < 2.3$			3.33	3.25	5.12	0.74	0.89

% Dev. = 100 ($P_{CALC} - P_{EXP}$)/P_{EXP}.

Han. Experimental uncertainties in the critical volume appear to be especially large for ethylene.

As seen in Tables 4 and 5, the BWR24 is increasingly less accurate above a reduced density of 1.8. To overcome this weakness, a second equation is developed by increasing the number of coefficients.

In order to fit a wider range of densities the following expanded form of the BWR equation is used:

$$Z = 1 + \left[B_0 + \frac{B_1}{T_R} + \frac{B_2}{T_R^2} + \frac{B_3}{T_R^3}\right]\frac{1}{V_R} + \left[C_0 + \frac{C_1}{T_R} + \frac{C_2}{T_R^2} + \frac{C_3}{T_R^3}\left(1 + \frac{C_4}{V_R^2}\right)\exp\left(-\frac{C_4}{V_R^2}\right)\right]\frac{1}{V_R^2} + \left[D_0 + \frac{D_1}{T_R}\right]\frac{1}{V_R^3} + \left[E_0 + \frac{E_1}{T_R}\left(1 + \frac{E_2}{V_R^4}\right)\exp\left(-\frac{E_2}{V_R^4}\right)\right]\frac{1}{V_R^4} + \left[F_0 + \frac{F_1}{T_R}\right]\frac{1}{V_R^5} \quad (3)$$

All coefficients in the equation are dimensionless and assumed to be quadratic with respect to the acentric factor except B_0, B_1, B_2, and B_3. Equation (3), which is referred to as BWR44 hereafter, has 44 constants whose numerical values are listed in Table 2b.

Table 6 shows the deviations between calculated and observed volumes above a reduced density of 1.8. The BWR44 is better than the other equations tested in this higher density region. It must be noted also that in the high pressure region fluids are relatively incompressible. Small errors in volume lead to very large errors in calculated pressures; therefore, at reduced densities higher than 1.8 it is not recommended that volume be used as an independent variable in BWR44. Conversely, if the independent variables are temperature and pressure as is usually the situation, then volumes can be predicted accurately. BWR24 and BWR44 are not designed for calculations involving the liquid phase, and no liquid data are used in determining the equation constants. Nevertheless, BWR44 does predict liquid volumes with an average deviation of about 1% and with maximum deviations of about 3% for a limited set of data tested.

Experimental errors comprise a substantial portion of the deviations reported in Tables 3 to 6. For example, Reamer et al. (1949) in comparing their data for propane with that of Beattie et al. (1937) found an average deviation of 0.22% in the measured pressures for 50 data points. Similarly in comparing six data points for *n*-pentane, Beattie et al. (1952) found an average deviation of 0.36% from the experimental results of Sage and Lacey (1942). These experimental deviations are comparable in magnitude to those recorded in Tables 3 and 6.

A good empirical equation of state should obey the following limiting condition:

$$\lim_{V\to\infty} V(Z-1) = B \quad (4)$$

where B is the experimental second virial coefficient. For BWR44 the second virial coefficient is

$$\frac{B}{V_{sc}} = B_0 + \frac{B_1}{T_R} + \frac{B_2}{T_R^2} + \frac{B_3}{T_R^3} \quad (5)$$

A comparison of Equation (5) with the second virial coefficient correlation of Pitzer and Curl (1957) shows that the two relationships are nearly comparable in accuracy.

ENTHALPY DEPARTURES

Equations for calculating enthalpy departures for BWR24 are provided by Edmister et al. (1968). Enthalpy departures from BWR44 are calculated as follows:

$$\frac{\Delta H}{RT_c} = \left[B_0T_R + 2B_1 + \frac{3B_2}{T_R} + \frac{4B_3}{T_R^2}\right]\frac{1}{V_R} + \left[C_0T_R + \frac{3}{2}C_1 + 2\frac{C_2}{T_R}\right]\frac{1}{V_R^2} + \left[D_0T_R + \frac{4}{3}D_1\right]\frac{1}{V_R^3} + \frac{E_0T_R}{V_R^4} + \left[F_0T_R + \frac{6}{5}F_1\right]\frac{1}{V_R^5} + \frac{C_3}{T_R^2V_R^2}\left[\frac{3V_R^2}{C_4} + \left(\frac{C_4}{V_R^2} - \frac{1}{2} - \frac{3V_R^2}{C_4}\right)\exp\left(-\frac{C_4}{V_R^2}\right)\right] + \frac{E_1}{V_R^4}\left[\frac{V_R^4}{2E_2} + \left(\frac{E_2}{V_R^4} + \frac{3}{4} - \frac{V_R^4}{2E_2}\right)\exp\left(-\frac{E_2}{V_R^4}\right)\right] \quad (6)$$

TABLE 5. THE 598 K ISOTHERM FOR *n*-HEPTANE
Data source: Smith et al. (1937)

ρ_R / V_{sc}/V	P_{EXP} [atm]	Z_{EXP}	% Deviation in Pressure: Original BWR	Generalized BWR	BWR24	Sugie and Lu	BWR44
0.4293	32.03	0.6525	0.18	0.92	0.40	−0.12	−0.13
0.6439	40.12	0.5449	−0.46	0.74	−0.00	0.14	−0.04
0.8586	46.38	0.4725	−0.47	1.19	0.29	0.58	0.61
1.0732	52.89	0.4310	0.27	2.34	1.20	1.04	1.04
1.2878	62.30	0.4231	0.61	2.98	1.37	1.15	0.49
1.5025	79.57	0.4632	−0.18	2.36	0.15	0.31	0.05
1.7171	114.24	0.5819	0.24	2.81	0.50	−1.42	−0.72
1.9318	183.67	0.8316	4.78	7.35	5.99	−3.32	−1.28
2.1464	315.73	1.2865	13.36	15.98	16.36	−4.26	−0.82
Avg. dev. $\rho_R < 1.8$			0.34	1.91	0.56	0.68	0.44
Avg. dev. $1.8 < \rho_R < 2.3$			9.07	11.68	11.23	3.79	1.04

% Dev. = 100 (P_{CALC} − P_{EXP})/P_{EXP}.

For a mixture the following combination rules of Kida and Gunn (1972) are used for both BWR24 and BWR44:

$$V_{scij} = \left[1 + 2.25\left(\frac{V_{sci}^{1/3} - V_{scj}^{1/3}}{V_{sci}^{1/3} + V_{scj}^{1/3}}\right)^2\right]\left(\frac{V_{sci}^{1/3} + V_{scj}^{1/3}}{2}\right)^3 \quad (7)$$

$$V_{scm} = \Sigma y_i y_j V_{scij} \quad (8)$$

$$\omega_{ij} = \frac{V_{sci}\omega_i + V_{scj}\omega_j}{V_{sci} + V_{scj}} \quad (9)$$

$$\omega_m = \Sigma(y_i y_j V_{scij}\omega_{ij})/V_{scm} \quad (10)$$

$$T_{cij} = (1 - k_{ij})\sqrt{T_{ci}T_{cj}} \quad (11)$$

$$T_{cm} = [\Sigma y_i y_j V_{scij} T_{cij}^2 / V_{scm}]^{1/2} \quad (12)$$

where k_{ij} is an interaction factor for a binary system. Values for k_{ij} have been tabulated by Chueh and Prausnitz (1968) for many systems of practical interest. The method of Hiza and Duncan (1970) or of Chueh and Prausnitz (1967) may be used to predict values for k_{ij} if binary volumetric data or tabulated values of the interaction constant are nonexistent.

In a recent study of enthalpy departure correlations the generalized method of Furtado et al. (1970) has been

Table 6. Comparison of Equations of State Above a Reduced Density of 1.8

Substance	T_R	Max. density (reduced)	No. of pts.	Avg. abs. dev. in vol., %* Methods (1)	(2)	(3)	(4)	Data source
Arbon	1.02-1.66	2.15	24	2.68	0.38	0.82	0.33	Michels et al. (1958)
Methane	1.07-2.48	2.51	28	1.81	0.27	0.89	0.55	Kvalnes and Gaddy (1931)
Ethane	1.02-1.56	2.35	27	0.63	0.46	0.52	0.26	Sage and Lacey (1950)
Propane	1.02-1.38	2.39	34	0.87	0.47	1.13	0.20	Sage and Lacey (1950)
Propane	1.00-1.01	2.00	2	0.85	0.47	1.22	0.54	Beattie et al. (1937)
n-heptane	1.01-1.20	2.44	34	0.96	0.50	1.43	0.29	Sage and Lacey (1950)
iso-butane	1.04-1.40	2.05	4	1.52	0.85	1.26	0.15	Beattie et al. (1950)
n-pentane	1.01-1.22	2.17	5	0.80	0.48	0.98	0.23	Beattie et al. (1952)
neo-pentane	1.00-1.27	2.18	8	2.97	2.04	0.49	0.79	Beattie et al. (1952)
n-hexane	1.01-1.13	2.21	11	3.40	3.13	2.32	1.44	Griskey and Canjar (1959)
n-hexane	1.03-1.08	2.02	5	2.36	1.68	1.32	0.08	Kelso and Felsing (1940)
Ethylene	1.06-1.50	2.83	19	2.13	1.09	2.23	0.81	Din (1959)
Propylene	1.02-1.16	2.83	24	1.19	0.35	2.62	0.57	Michels et al. (1953)
n-heptane	1.02-1.15	2.14	7	1.80	0.65	1.65	0.18	Smith et al. (1937)
Carbon dioxide	1.03-1.39	2.60	59	1.16	0.41	3.10	1.11	Din (1959)
Hydrogen sulfide	1.01-1.19	2.20	6	0.52	0.56	2.02	1.48	Sage and Lacey (1950)
Nitrogen	1.35-3.17	2.74	10	0.78	1.93	0.89	0.17	Din (1959)
Grand avg. dev.			307	1.55	0.92	1.46	0.54	

* % Dev. = 100 ($V_{EXP} - V_{CALC}$)/V_{EXP}.
Methods: 1. Generalized BWR of Edmister et al. (1968).
2. Sugie and Lu (1970, 1971).
3. BWR24.
4. BWR44.

Table 7. Deviations in Enthalpy Departure Calculation
Data source: Starling et al. (1971)

System	k_{12}	No. of pts.	Dev., joules/g BWR24	BWR44	Furtado et al.
n-octane	—	42	0.84	1.30	0.71
Methane	—	20	2.84	1.21	0.92
n-pentane	—	125	4.27	4.31	3.47
cyclo-hexane	—	82	3.26	2.89	3.43
n-octane	—	37	8.62	12.22	7.20
56.6% methane—43.4% nitrogen	0.03	45	1.51	1.34	0.50
94.8% methane—5.2% propane	0.02	27	1.42	2.18	0.96
88.3% methane—11.7% propane	0.02	26	0.96	1.30	0.79
72.0% methane—29.0% propane	0.02	21	1.80	2.26	1.59
49.4% methane—50.6% propane	0.02	16	2.97	3.60	3.51
23.4% methane—76.6% propane	0.02	8	3.64	4.69	1.92
79.3% *n*-pentane—20.7% cyclo-hexane	0.00	107	2.38	2.26	3.14
61.2% *n*-pentane—38.8% cyclo-hexane	0.00	101	3.35	3.43	4.14
38.5% *n*-pentane—61.5% cyclo-hexane	0.00	102	3.10	3.43	3.47
19.7% *n*-pentane—80.3% cyclo-hexane	0.00	91	5.40	5.40	6.07
80.9% *n*-pentane—19.1% *n*-octane	0.00	45	7.36	7.20	9.16
59.7% *n*-pentane—40.3% *n*-octane	0.00	49	5.81	5.65	8.91
39.2% *n*-pentane—60.8% *n*-octane	0.00	36	5.23	6.15	10.50
21.8% *n*-pentane—78.2% *n*-octane	0.00	38	8.36	7.82	6.77
Average deviation		1018	3.81	4.10	4.10

found to be the best among those tested although several other methods were found by Starling et al. (1971) to be nearly as accurate. For this work the method of Furtado et al. (1970) is used as the standard for comparison with the predictions of BWR24 and BWR44. Table 7* shows that BWR24 and BWR44 are at least as accurate for the gas phase as the Furtado method. The proposed equations are slightly less accurate for pure components but somewhat superior for mixtures.

Finally it is emphasized that the constants in Table 2 are determined from compounds with acentric factors no larger than 0.35 because vapor phase high density data are nearly nonexistent for substances with a larger ω. The constants in Table 2 are quadratic in the acentric factor, and extrapolation of second-order functions is usually unreliable except over narrow ranges.

NOTATION

B = second virial coefficient
ΔH = enthalpy departure
k_{ij} = binary interaction factor
P = pressure
R = gas constant
T = temperature
T_R = reduced temperature $= T/T_c$
V = volume
$V_{0.6}$ = saturated liquid volume at $T_R = 0.6$
V_R = reduced volume $= V/V_{sc}$
V_{sc} = scaling volume
y = mole fraction
Z = compressibility factor

Greek Letters

ρ = density
ω = acentric factor

Subscripts

c = property at critical point
calc = calculated property
exp = experimental measurement
i, j = components i and j respectively
m = property for a mixture
R = reduced property

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* Enthalpy departures calculated from the equation of Starling and Han (1972) show average deviations about twice those reported in Table 7 for BWR24.

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